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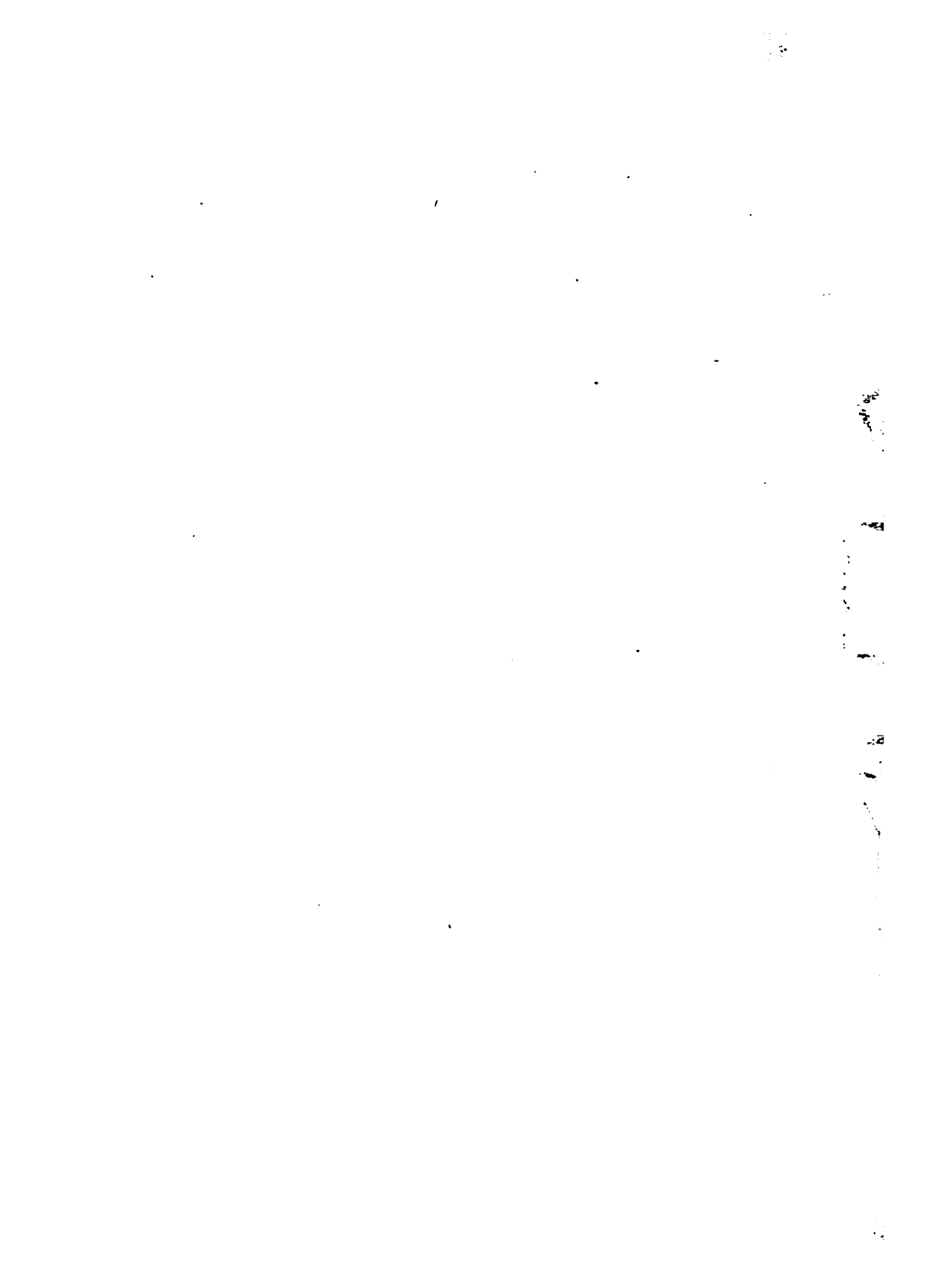
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CALCAREOUS CEMENTS:

THEIR NATURE, MANUFACTURE, AND USES.

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CALCAREOUS CEMENTS:

THEIR NATURE, MANUFACTURE, AND USES,

WITH

SOME OBSERVATIONS UPON CEMENT TESTING.

BY

GILBERT R. REDGRAVE,
ASSOCIATE OF THE INSTITUTION OF CIVIL ENGINEERS,

AND

CHARLES SPACKMAN,
FELLOW OF THE CHEMICAL SOCIETY.

With Sixty-Three Illustrations.

SECOND AND REVISED EDITION.



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PREFACE TO THE SECOND EDITION.

ONE of the authors, in the preface to the former edition, expressed his fears for the future of the cement industry in this country, and pronounced the opinion that the trade was about to enter upon a very critical period. Since these views were recorded we have seen the establishment of the great combination of English manufacturers and the important changes in the industry due to the introduction of the rotary kiln and the tube-mill. Nearly all the plant which was regarded as essential ten years ago has now become obsolete, and the processes of manufacture have undergone such a complete revolution that it has become necessary to re-write entire chapters, descriptive of the appliances in common use at that date. The authors have attempted in what follows to give a true description of the altered methods which now prevail in the production of Portland cement, and they have endeavoured to set before the reader a faithful account of all the most recent processes adopted in this country, as also in the United States and on the Continent, where the cement manufacture has developed to an amazing extent.

It is only by the most fearless sacrifice of antiquated methods and obsolete machinery that cement makers in this country can hope to compete with their foreign rivals. We are still far from realising what can be accomplished from cement rightly and intelligently used, and we are convinced that we are merely on the threshold of the great increase in the demand for this material which will take place when the engineer has fully grasped the enormous possibilities of "armoured" and "re-enforced" concrete construction.

Many doubtful matters in the chemistry of cement action are now in course of being rendered clear, and, in the hands of skilful

and competent chemists, the problems which still require solution are daily being explored with success. We have placed on record some of the theories of cement reactions which have been promulgated by English and foreign experimenters, and we have considerably added to our former Chapter on the Analysis of Cement Mixtures. We trust that by this means we have been able to bring up the knowledge of the chemistry of the subject to current requirements, and that our work will be found useful both in the laboratory and in the manufactory.

The authors desire to express their best thanks to the manufacturers and others who have supplied them with valuable information and assistance. They are also indebted to Messrs. Lathbury & Spackman, The Conveyor and Elevator Co., Messrs. Bagshawe & Co., Messrs. R. Broadbent & Son, Ltd., The Bradley Pulverizer Co., Messrs. T. L. Smidth & Co., Messrs. C. Whittaker & Co., Ltd., Messrs. Hadfield's Steel Foundry Co., and Mr. Patrick Adie, for the loan of blocks and other illustrations.

GILBERT R. REDGRAVE.
CHARLES SPACKMAN.

THRIFFWOOD,
SYDENHAM, S.E.

PREFACE TO THE FIRST EDITION.

THE marked improvements effected in recent years in the use of limes and cements date back undoubtedly to the close of the last century. They may be ascribed, partly to the great advance made about that time in chemical and scientific knowledge, and to the accurate habits of thought and practical research induced by the spread of that knowledge, partly, also, to the rapid growth of engineering skill, which characterised that period.

In both of these directions our own countrymen yielded important services, and, so far as limes and cements are concerned, while the "ingenious" Dr. Brindley Higgins was about 1780 laying the foundations of a proper study of the chemistry of the subject, Smeaton had already, as early as 1756, observed the notable fact that the hydraulicity of limes was due to the presence in them of clay.

The records of the English Patent Office do not, however, disclose any great activity in these branches of invention until thirty or forty years later, and considerable progress appears to have been made in the manufacture of artificial limes abroad, before the subject attracted serious attention in England. The discovery by Parker of the valuable cement made from the septaria of the London clay, patented by him in 1796, was doubtless an invention of the utmost importance, as I shall attempt to show, when dealing with the subject from the historical point of view.

Little injustice will probably be done to those who have turned their attention to these materials, if we state that from the times of the Romans until Smeaton's discovery—say for a period of close upon two thousand years—no substantial advance was made in the employment of limes and cements. It has, in fact, been reserved for the latter half of the nineteenth century to demonstrate the superiority of artificial cements over the best descriptions of natural cements and admixtures of fat or pure limes with other substances imparting to them cementitious properties.

Notwithstanding the excellence of the cements now being placed upon the market, and the amount of attention which the manufacture and employment of cements have recently received, we have still much to learn respecting the chemistry of cement

action, and concerning the problems involved in the economical production of these materials. On the subject of testing cements we are, be it confessed, lamentably deficient, as compared with many of our Continental neighbours, and in this direction, more especially as regards the introduction of some uniform and generally accepted system of testing, there is still much to be accomplished in England.

It has seemed to me, therefore, that a brief account of the history of the employment of cement in the past, which has received but little attention from previous writers, together with a description of the various processes of the manufacture, might be of use at the present time. I have also collected some of the opinions of experts on the testing of cement, and I have appended a full translation of the German Rules for Testing, which, I think, have not previously been published in this country. These rules would appear to possess peculiar interest at the present time, in consequence of the controversy which has arisen among English manufacturers, even while this work is passing through the press, concerning the nature of Portland cement. The question of the legality or otherwise of the mixture with the cement, during the process of grinding, of less valuable ingredients was fought out in Germany more than twelve years ago, and after careful consideration and many experiments, it was decided both by manufacturers and engineers to adopt such a definition of "Portland cement" as to exclude all such admixtures, except two per cent. of plaster of Paris, employed for a special purpose. With the reasons for this use of plaster I have dealt fully in the ensuing pages, and the question whether Kentish ragstone or any other variety of unburnt material, or slag, should be employed by the manufacturer, would seem properly to come within the provisions of the Adulteration Acts, when we have such an extension of these Acts, as is, I believe, contemplated.

I cannot claim to have dealt with the subject exhaustively, but I have endeavoured to represent the present aspect of the cement question impartially, not only from the point of view of the manufacturer, but also from that of the cement user, in both of which directions I have had the advantage of a practical acquaintance with the facts to which I refer.

The leading works on limes and cements, both in this country and abroad, have been freely consulted and laid under contribution,

and I have endeavoured in all cases to acknowledge my obligations to the writers whose opinions I have quoted. I have availed myself extensively of the *Minutes of Proceedings of the Institution of Civil Engineers*, which contain some of the most valuable essays on Portland cement in existence, and I have here to tender my special thanks to my colleague, Mr. Charles Spackman, F.C.S., who has prepared the greater part of the Chapter on Grinding Machinery, and the original and important Chapter on the Chemical Analysis of Cements and Cement Materials. Many other manufacturers have likewise aided me largely with facts and figures, and I wish also to record my indebtedness to Mr. I. C. Johnson for much valuable information.

I trust that this account of what has been achieved in the past, and this brief record of the present state of our knowledge of limes and cements may be useful to those who may come after, and to all engaged in this branch of industry.

I regard the present time as, in many respects, a very critical period in the history of the cement trade. Our own country, the original seat of the manufacture, has been distanced in certain directions in consequence of the superior scientific skill and the energy of foreign rivals. The supremacy we have so long enjoyed has undoubtedly been to some extent wrested from us by the products of Continental industry and enterprise, and in the absence of some united action and some intelligent leading, our manufacturers are threatened with a competition which they are not adequately armed to encounter.

It would be idle on my part to deny that I dread times of even greater depression than those we have hitherto experienced in this important industry, and I am convinced that nothing but the formation of a powerful confederation of cement producers and cement users, such as exists in many of the most enlightened countries abroad, will extricate us from the difficulties by which we are surrounded. I trust that it may be possible to induce the Institution of Civil Engineers or some influential Corporation to undertake these duties, and to free us from the dangers which I have attempted to indicate.

GILBERT R. REDGRAVE.

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CALCAREOUS CEMENTS:

THEIR NATURE, MANUFACTURE, AND USES.

CHAPTER I.

INTRODUCTION.

CONTENTS.—Antiquity of use of Lime—Definition of Limes and Cements—Slaking—Quicklime—Chemistry of Limes and Cements—Action of Carbonic Acid—Silica and Alumina—Calcination of Limes—Hydration—Influence of Alkalies.

Antiquity of the Use of Lime.—The practice of employing limes as binding agents for stones, bricks, and other similar materials used in construction is one of great antiquity, and the Romans, the most mighty builders of the ancient world, were well acquainted with the use of limes, as also with certain of the methods of improving fat or pure limes, in order to impart to them cementitious and hydraulic properties.

Definition of Cements and Limes.—"Cements," as distinguished from limes, are materials which are capable of solidifying when in contact with water without perceptible change of volume, or notable evolution of heat; "hydraulic cements and limes" are such as possess the power of "setting" or solidifying under water. All limes have a tendency to expand and to fall asunder, or to crumble into powder when treated with water, and are said to become "slaked." The purer the lime the more energetic and rapid is this action, while conversely the greater the quantity of clayey matter combined with the lime, the less intense, as a rule, is the chemical affinity for water, and the slower is the act of hydration, and to this extent the greater is the resemblance of such limes to cements. "Limes," therefore, as distinguished from cements, "fall" or crumble when exposed to the action of water.

It may be as well to point out here that the above definitions, though they do not entirely accord with all the previous theories of limes and cements, are those which will be adopted in the present work.

Combination of Lime with Water.—The chemical affinity of lime for water is one of the most powerful with which we are acquainted, and "quicklime" (calcium oxide), or lime recently calcined, when exposed to the air speedily attracts moisture from the atmosphere, and combines with such water to form calcium hydroxide, or slaked lime. This hydroxide may occupy as much as three times the space previously filled by the quicklime, and therefore the amount of slaked lime produced from a given bulk of quicklime appears, in certain cases, to be very considerable.

The Speed of Slaking.—Some writers have attempted to classify the different varieties of lime in accordance with the quantity of slaked lime produced, or with the speed with which they were observed to combine with water; but it is now known that this slaking action depends upon numerous conditions which have to be specially studied for each class of limes, and that any general deductions founded upon the act of hydration alone are likely to be inaccurate and misleading.

Intermediate Limes.—Certain impure limes, resembling in their composition the constitution of cements, have been appropriately named "intermediate limes," or such as occupy a position intermediate between the true limes, which undergo disruption when exposed to the action of water, and the cements which do not, apparently, become changed when so treated.

It may be assumed that limes of every different degree of energy, from pure oxide of calcium down to true calcareous cements, exist in nature; thus there is an enormous range of varieties of action to be studied, and any attempt to classify all limes under two or three sub-heads must be futile and untrustworthy.

In order to rightly understand the action of limes and cements, a certain amount of chemical knowledge is involved, and this branch of the subject may now be briefly discussed.

Quicklime or Caustic Lime.—Quicklime, caustic lime, or the oxide of calcium, one of the earthy metals, does not exist in nature, nor is metallic calcium itself anywhere found in an uncombined form. We obtain quicklime, the chemical symbol for which is CaO , by calcining or heating to redness a carbonate of lime, CaCO_3 , and by this means expelling the carbonic acid gas or carbon dioxide, CO_2 , with which the lime is combined, and which can be driven off in the gaseous form at a cherry-red heat (about 440° Centigrade).

Preparation of Quicklime.—Lime combined with carbonic acid is found in a great variety of rocks in all parts of the world, and in every different degree of purity. From any pure carbonate of lime, such as marble, or from any of the various descriptions of limestone and of chalk, the calcium oxide or quicklime can thus readily be prepared; but

in order to keep the oxide unchanged, it must, as already stated, be preserved from contact with the atmosphere.

Chemical Composition of Quicklime.—In a pure carbonate of lime 44 parts by weight of carbon dioxide or carbonic acid are combined with 56 parts by weight of calcium oxide. In the oxide itself 40 parts by weight of metallic calcium, Ca, are combined with 16 parts of oxygen gas, O. This oxide cannot be decomposed by heat. The lime burner has, therefore, in his kilns to drive off the combined carbonic acid in the form of a gas, and thus to obtain the lime as used by the builder.

Calcination of Limestone.—Generally speaking, the limestone or chalk, when placed in the kiln, contains a certain percentage of moisture, which has also to be expelled, and thus the lime burner can rarely, when the stone is thoroughly well burned and all the carbon dioxide is expelled, obtain more than half its weight of quicklime from a given weight of stone dealt with in the kiln, though in theory the yield should be 56 per cent. of lime.

Carbonic acid gas is driven off much more freely in an atmosphere of steam, and for this reason some authorities have advised the use of the steam jet in lime kilns, but we are not aware that this plan has met with any measure of practical success.

Action of Aqueous Vapour.—The action of aqueous vapour upon the lime undergoing calcination may be thus explained:—A vapour or gas ascends into a space already occupied by another gas differing from it in composition, almost as quickly as it would into a vacuum, owing to the law of the diffusion of gases, which teaches us that the various gases have such a powerful tendency to permeate each other, that, in order to do so, they will frequently overcome considerable resistance. Water, for example, evaporates as readily into dry air as into a vacuum, but this tendency is impeded when the air above it is already charged with aqueous vapour. In the same way when the red-hot lime is giving off carbonic acid gas, this gas escapes much more freely into an atmosphere of aqueous vapour than into one of carbonic acid gas, for in this latter case the escaping carbonic acid has to overcome the pressure of that which has been already evolved. It is true that if we could substitute a current of air at a very high temperature for the aqueous vapour the result would be the same, but this would entail practical difficulties.

Gay-Lussac's Experiment.—Gay-Lussac, the eminent chemist, devised an ingenious experiment to demonstrate the effect of steam upon the calcination of lime. He introduced into a hard glass tube, inserted in a furnace which enabled it to be raised to the required temperature, some pieces of broken marble. One end of the tube was connected with

an apparatus for the evolution of steam, and the other end was furnished with a contrivance for collecting the carbonic acid gas. The temperature was then raised to the point at which the marble began to be rapidly decomposed, and at this stage by checking the draught the mass was reduced to a dark red heat, so that all evolution of carbonic acid ceased. Steam was at this moment permitted to pass through the tube, and at once carbonic acid gas again made its appearance in considerable quantities and continued to pass off under these circumstances in a manner entirely dependent upon the current of vapour. This experiment proves that limestone is decomposed at a far lower temperature with the help of aqueous vapour than under ordinary circumstances. In an atmosphere of carbonic acid gas, carbonate of lime, as we know from the investigations of Faraday and Hall, remains unchanged even at a full red heat.

Composition of Slaked Lime.—When lime becomes “slaked” it is found that 56 parts by weight of quicklime combine with 18 parts by weight of water, H_2O , to form 74 parts of calcium hydroxide, $Ca(OH)_2$. Great heat is evolved in this process, and the action is expedited by the use of boiling water. Certain “poor limes” which will scarcely slake or fall to powder when cold water is employed, will crumble into dust readily if the water is at the boiling point.

Classification of Limes.—Limes are frequently classed as “fat” or rich limes, if they readily become slaked and furnish a large volume of powder, and “poor” if they are impure and become slaked slowly, yielding relatively but little dust. Cases occur, of course, when the lime will not fall or slake at all. Certain poor limes, which are practically natural cements, may, if they are calcined at a proper temperature and are finely ground, be employed as cements. To render these limes available for the use of the builder, it is thus necessary that they should be ground previous to use.

Condition of Water in Slaked Lime.—The water which combines with the lime in the act of hydration is truly solidified, and the hydrate formed is, when the exact proportion of water necessary for this purpose has been employed, an absolutely dry powder. On adding a further quantity of water, the bulk of this powder is much reduced, and it may be tempered into an extremely rich and unctuous paste. If this paste is permitted to dry, it shrinks and forms a porous mass of no great hardness.

Dry Slaked Lime kept from Air remains unchanged.—If the hydrate of lime is preserved from atmospheric action and placed in a hermetically sealed vessel, either as a dry powder or made up with water, it undergoes no alteration whatever, the powder remaining as such for an indefinite period, and the paste showing no sign of change. The hydrate

of lime possesses in fact no inherent power of solidification. In proof of this Alberti states that some lime taken from a mortar-pit in an old ditch, abandoned for upwards of 500 years, was "still so moist, well tempered, and ripe that not honey or the marrow of animals could be more so."

Lime slowly recombines with Carbonic Acid.—When exposed to the air, pure caustic lime is converted very slowly and without notable increase of temperature into a rather coarse powder. It is not, under these circumstances, wholly converted into a carbonate of lime, even after the lapse of many years, but, by the simultaneous absorption of moisture and carbonic acid, it is resolved into a double compound having the formula, according to Fuchs, of $\text{CaCO}_3 + \text{Ca}(\text{OH})_2$, or consisting of equal equivalents of the carbonate and the hydrate of lime. The carbonate thus produced would seem to result from the decomposition of the first-formed hydrate, for when moisture is wholly excluded no combination between the lime and the dry carbonic acid gas takes place. In order to expel the water of hydration, the slaked lime must again be heated to dull redness.

The Action of Carbonic Acid mainly Superficial.—Lime made from pure carbonate of lime, when slaked and used for mortar, likewise gradually recombines with the carbonic acid gas present in the atmosphere and becomes indurated, but this action is mainly in the superficial layers of the mortar, as the gas penetrates very slowly. In fact years must elapse before the recarbonisation of the lime is thoroughly accomplished, and in the case of thick walls the internal layers of mortar never become completely hard. It is necessary to distinguish between the so-called "set" of the mortar, which is merely due to the absorption of the superabundant water, and the actual induration by means of the carbonic acid gas which is a process of years or of ages in the case of pure limes.

The Influence of Clayey Matters.—But absolutely pure limestones are only met with in exceptional cases, as nearly all limestone rocks, and the greater part of the chalk formation contain varying percentages of clayey matters (silicates of alumina), iron, alkalies, &c., and it is upon the proportion of these ingredients present that the behaviour of the calcined lime principally depends. It is, in fact, owing to the presence of certain of these clayey matters, first, as we shall see pointed out by Smeaton, that limes pass over by gradual stages into the form of cements; that is to say, that these substances so far influence the slaking action that they may even bring about the ultimate setting of the mixture without change of volume—the characteristic property (as already stated) of cements.

Artificial Admixture of Clayey Matters.—It is not necessary,

however, that the limestone should have been the source from which these clayey matters were derived; they may be conveyed to the calcined lime by admixture with it at the time when it is treated with water, or they may be ground up along with the lump lime before it is slaked. It is this fact which needs careful consideration when we have to deal with the influence of heat on mixtures of lime and clay, and the nature of the changes effected in the kiln. The silica compounds are of a very complex character, and may be produced, as we shall see, both by heat and in the humid way. All that is necessary for the due action of these clayey matters is that they should themselves have been roasted or calcined, either artificially or by volcanic heat.

Puzziolana, Trass, &c.—Certain of these substances which are added to pure limes to bring about this action are called puzzuolanas or trass. These are clayey or siliceous matters of volcanic origin, but roasted shales, brick dust, and burnt clay or ballast, all of them, more or less, possess this influence on the pure limes, and have the power of imparting to them the attributes of cements.

The volcanic ash found in the island of Santorin, and known as Santorin earth, is typical of many kinds of scorïæ which have been used successfully with fat or pure limes to impart to them hydraulic properties. The proportion of silicate of alumina in this substance is relatively high, and there is much less iron than in the case of trass and puzzuolana.

Silica and its Compounds.—It will be necessary, in order to understand the chemistry of cements, to treat next of silica and its compounds. Silica, the oxide of the element silicon, is found very widely distributed in nature, sometimes pure but more often in combination with other substances, as it possesses strong affinity for entering into the composition of complex salts, known as compound silicates. It plays the part of an acid, and combines with lime, alumina, iron oxides and the alkalies in numerous different proportions. It is found that 28 parts by weight of silicon, Si, and 32 parts by weight of oxygen are present in silicic acid or silica, having the chemical formula of SiO_2 . Clay, the silicate of alumina, may be taken as the type of the silica compounds, while quartz, flint, and chalcedony consist of almost pure silica. Porcelain clay, which contains about 47 parts per cent. of silica, 39.2 parts of alumina, Al_2O_3 , and 13.7 parts of water, and corresponds to the chemical formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{Aq}$, with a molecular weight of 258.4, may represent the silicates. There are, however, an enormous number of clays in which silica and alumina are present in very varying proportions, and which contain in addition iron oxides, alkalies, lime, &c. For certain of these clays it becomes almost impossible to propound any reliable chemical formula, to express their composition; and alumina, while it

may combine in certain definite proportions with the silica as a base is also capable of acting as an acid, and of combining with lime and the alkalies to form certain more or less unstable compounds termed aluminates.

Alumina is the oxide of the metal aluminium, Al, which has the atomic weight of 27.2, and two parts of aluminium combine with three parts of oxygen, equal to 48, to form its only known oxide, termed alumina, the molecular weight of which is 102.4.

It will not now be necessary to study in detail the combinations of silica and alumina with iron oxides and the alkalies—soda and potash—though these compounds play a very important part in cement action; we shall have to revert to this question hereafter when we consider the chemical changes consequent on the calcination, the hydration and the induration of cements of various kinds.

Restricting ourselves for the present, therefore, to the silicates of alumina as typical of the compounds of silicic acid, we may pass on to discuss the modifications brought about in the slaking action of limes consequent upon the presence of these substances. We will take first impure limestones, or such as contain a proportion of the silicate of alumina, together with certain percentages of the oxides of iron tending to discolour the lime.

Influence of Heat on the Silicates.—When limes of this character—namely, such as are combined with varying percentages of silicates—are burnt in the ordinary way in the kiln, the carbonic acid gas is first expelled from them, as in the case of the pure limestones, and the clayey matters assist in its expulsion, owing partly to the affinity of the silicic acid for the lime and partly to the fact that the free and combined water in the clay is driven off, and the steam produced in this way facilitates, as already stated, the expulsion of the carbonic acid. There is thus a double change to be effected in the kiln, and the expulsion of the water from the hydrated silicate of alumina in the clay may go on side by side with the dispersal of the carbonic acid.

The Calcination of Clayey Limestones.—These clayey limestones are thus burnt more readily than the pure limestones; they also require less fuel and less time. But when the heat is sufficiently prolonged, a further action takes place in the kiln, the silicic acid and the lime react upon one another, and either produce a new compound, termed silicate of lime, or so far further the formation of such a silicate that, on the addition of water, this compound is formed with great rapidity. The silica combined with alumina and iron oxides in the clay passes to the lime when the carbonic acid is expelled, and no doubt portions of the silica are seized upon by the red-hot lime, which is in what chemists term the “nascent state,” and is, therefore, in a condition eminently well fitted to

form fresh chemical compounds. Similarly the alumina and the iron oxide act as feeble acids, and combine with a portion of the lime to form aluminates and ferrites of lime at the temperatures found in the cement kiln. The calcined mass, if it is then brought into a very finely-divided condition, can readily be acted upon by water.

Action of Water on Silicates formed in the Kiln.—In using, for structural purposes, limes of this character, therefore, a fresh set of affinities comes into play. We have, first, the affinity of the quicklime for water, and, secondly, the affinity of the hydrate of lime and the silica and alumina to enter into combination. It must be pointed out that this second reaction can and does greatly change the violence of the affinity of lime for water, and that it is possible to so "deaden," if we may thus term it, the action of quicklime that, upon the addition of water, instead of heating up and falling into powder, it may pass (as we have seen) into the condition of a hydrated silicate, without perceptible heat, and with little or no change of physical condition.

Stable Compounds formed by Hydration.—The hydrated silicates of lime thus produced are not liable to be altered to any appreciable extent when exposed to the prolonged action of water or of the atmosphere, and the compounds of lime with silica and alumina thus afford a durable cementing material, suitable also for hydraulic purposes. It must not be forgotten that the lime which enters into combination with the silicic acid passes from a slightly soluble into an almost completely insoluble condition, and it will be observed that the action of induration differs entirely, in the case of cements, from the slow and tedious hardening of common lime mortar, due to the gradual recombination of the lime with the carbonic acid gas present in the atmosphere.

Character of the Kiln Changes.—It will have been noticed that we were careful to state that the lime, as also the silica, the alumina, and the iron oxides, either entered directly into fresh chemical combinations, or that they tended to promote the formation of silicates and other compounds; for the changes brought about in the kiln, and the subsequent reactions which take place when water is added to the calcined materials are very complex and difficult to investigate. It is evident from very simple tests that, even in the case of cements of the Portland type, considerable quantities of lime remain in a condition under which they are capable of combining immediately with water, or in a state in which such lime is free to be acted upon or to undergo further chemical change. In a well-burnt sample of intermediate lime the silica has assumed that form in which it is soluble in a boiling solution of carbonate of soda, after treatment with hydrochloric acid, for clay which has been calcined in contact with lime or other metallic oxides is readily attacked by the acid, and the silica liberated assumes

the gelatinous condition, or that in which it can freely combine with the alkalies. During the calcination, therefore, of hydraulic limes a stage is reached when, after the expulsion of the carbonic acid, the silica and the alumina of the clay on the one hand and the lime on the other are in a condition to mutually react upon one another, and to form compounds capable of being re-arranged in the presence of water. The most recent opinion is that in well-made samples of Portland cement we have a tri-calcium silicate in conjunction with a tri-calcium aluminate. If a small quantity of the lime is combined with the iron oxide as a calcium ferrite, these compounds would together account for the whole of the lime present in the original mixture. We are not able to state very definitely the proportions of these combinations, but this fact is certain, that at this period of the calcining process a very slight increase of heat suffices to fuse or partially vitrify the mass, in which case complete combination between the lime and silica has undoubtedly taken place, and the silicates produced in this way by heat manifest but little tendency to undergo any change when treated with water. It is, therefore, most important not to overburn or, as it is termed, to "clinker" these intermediate limes, though in the manufacture of Portland cement it is essential that the stage of incipient fusion should be attained in the kiln.

Action of Impure Limestones when Calcined.—Some clayey limestones are much more liable to fuse than others, and it has been pointed out that those in which the proportion of iron oxide and of alkalies is large are most exposed to this risk. The glass-like or vitreous silicates formed in this way by heat are generally produced only on the surface of the lumps of overburnt lime, and unless such lumps are carefully picked out and cast aside when the lime is being made into mortar, they may be the source of much subsequent injury to the work, first by the retarded slaking of particles of lime encased in the inert silicates, and second by the more gradual hydration of certain of these complex silicates which may be attended by slight increase in bulk, tending to the disruption of the mass.

Limes vary widely in their behaviour with Water.—It will be understood that, between the pure or fat limes, which slake in the ordinary way, and the true cements which set without change of volume, there are an infinite number of varieties of limes which incline in one direction or the other towards these two extremes. There are also numerous hydraulic limes which first fall to pieces during the act of hydration, and which subsequently set and become indurated when the effect of the silicates comes into play. To this category belong many of the limes of the lias formation, and certain of the grey limes of the lower chalk.

Definition of the Energy of Cement Action.—The energy of a cement depends upon the rapidity with which the lime and the silica, or the lime and the alumina, combine in the presence of water to form stable compounds, or with which the ready-formed silicates and aluminates become hydrated when water is added. We have thus the quick-setting cements of the Roman cement type, which become indurated mainly by simple hydration in a few minutes, and the dense cements resembling Portland, which depend for their induration on a re-arrangement of the silicates, and which may take as many hours to set as the former substance does minutes.

It should be here noted that when we speak of the setting of cements we imply the act of induration and not the mere absorption of the water, which is most characteristic of the imperfect setting action of a lime mortar.

The Influence of Calcination upon Cement Action.—The calcination of these varieties of cements plays a very important part in their subsequent behaviour, when tempered with water. Thus it is possible from the same clay-limestone to prepare

- (a) A hydraulic lime ;
- (b) A quick-setting cement ; and
- (c) A cement resembling Portland cement in character.

At a low temperature in the kiln the mixtures of lime and clay have not mutually reacted the one on the other, and we obtain a material in which the energy due to the hydration of the lime overcomes the tendency of the silicic acid to enter into combination with this lime, under the agency of water.

When the second stage in the calcination is reached the silicic acid is liberated or rendered capable of attacking the lime, yielding a cement which sets with comparative rapidity. While, lastly, under still more intense firing, the stage of calcination is approached when silicates and aluminates are formed in the kiln and when the material acts like a Portland cement, and when the iron, moreover, which had during the first and second degrees of calcination remained in the condition of a peroxide, passes into that of a protoxide (as is always the case in perfectly prepared Portland cement). This change in the oxide of iron is only effected at very high temperatures, and furnishes a certain indication of the production of a dense slow-setting cement. If, in the case of this clayey limestone, the clay had been less in quantity we should have obtained a hydraulic lime which would slake with difficulty, and which would be liable to the evil effects of "after-slaking." If the proportion of the bases contained in the clay, relatively to the amount of silicic acid present, had been greater, the mass would have probably become vitrified

or partially fused before the temperature necessary for the final stage of calcination was reached.

Condition of the Silica Important.—The condition of the silica present in impure limestones has an important influence on their value when employed for the manufacture of hydraulic lime. Any silica existing in the uncombined state as quartz sand is unacted upon by the lime at the comparatively low temperature of the kiln, and consequently after calcination it does not separate as a gelatinous bulky mass, as is usual with the silica in samples of hydraulic lime, when treated with hydrochloric acid. Further, it is unacted upon by a boiling solution of sodium carbonate, and it is not in a condition to enter into combination; it is present, in fact, simply as inert matter. In order to confer hydraulic properties upon the lime much of the silica must, before burning, occur in combination, preferably with alumina.

Many of the beds of impure limestone in the carboniferous deposits contain free silica as sand in considerable quantity. Lime prepared from stone of this description is easily recognised by its friable granular appearance, while, on the other hand, that which is burnt from stone in which the silica exists in combination with other substances, as is the case in the beds of the lias formation and in some of the carboniferous deposits, has a dense, close, even structure; the lumps of quicklime ringing when struck together.

Analyses of Hydraulic Limestones and Lime.—The following are analyses of blue lias hydraulic limestones of excellent quality, No. 1 being from the neighbourhood of Newport, Monmouthshire, and No. 2 from Leicestershire:—

	No. 1.	No. 2.
Silica,	7·311	9·680
Alumina,	2·315	2·827
Ferric oxide,	·530	·563
Iron disulphide,	1·149	·370
Calcium carbonate,	83·095	82·128
Calcium sulphate,	·275	2·122
Calcium phosphate,	·087	...
Magnesium carbonate,	3·605	·134
Potash,	·597	} Not determined.
Soda,	·318	
Loss on ignition,	·834	
	100·116	97·824

The following are analyses of the blue lias hydraulic lime of Leicestershire, No. 1 ground, No. 2 lump. The beds of stone burned for the preparation of the ground lime contain more clay than those used for the lump lime, and, after burning, the lime would either slake with

difficulty, as described in the preceding paragraph, or it might not slake at all. When ground and stored for a short time, the material possesses the properties of a cement, setting and hardening without perceptible alteration in volume. Both of these limes have attained a deservedly high reputation as water limes:—

	No. 1	No. 2.
Insoluble siliceous matter,	3·603	1·031
Silica,	17·496	12·230
Ferric oxide,	8·972	2·907
Alumina,	5·120	4·640
Lime,	57·393	72·980
Magnesia,	·618	2·479
Sulphuric acid,	3·153	1·775
Potash,	·862	·641
Soda,	·346	·203
Loss on ignition,	2·480	1·062
	100·043	99·948

The Influence of the Alkalies.—We have still to deal with the alkalies and their combinations as affecting cement action in conjunction with lime. The proportion of alkaline matters present in the clay used for cement varies, as we shall see later, very considerably; but the presence of the alkalies is of the utmost importance to the cement manufacturer, for many of the chemical changes upon which he relies are largely assisted by the formation of alkaline compounds. It must be remembered that the potassium and sodium silicates are the only ones which are soluble, and the alkalies therefore act as carriers of the silicic acid to the lime and the alumina in the presence of water. Moreover, it is, as already stated, a well-known chemical fact that silica when acting as an acid has a great tendency to enter into combination with a group of bases rather than with any single substance. It is probably for this reason that compound silicates of lime, alumina, iron, and the alkalies are so readily formed in the kiln.

Fremy's Experiments.—From the experiments of M. Fremy, to which we shall refer at considerable length when we consider in detail the kiln changes during the calcination of Portland cement, it appears that lime and silica react upon each other at a much lower temperature than lime and alumina; silicates of lime being produced at temperatures below 700° Centigrade (1,292° Fahrenheit); while the alumina and lime or the silicate of lime and alumina only begin to form double compounds when that temperature is exceeded. The heat of the kiln at which incipient fusion takes place is about 1,600° Centigrade (2,912° Fahrenheit). It seems, however, probable that alkaline matters have the property to influence the reaction of the

lime, alumina, and silica, as also that of the iron oxides, in the cement-material at much lower temperatures, acting in the nature of fluxes, and we think that the knowledge derived from experiments with lime and silica, or lime, silica, and alumina in the absence of the alkalies, is liable to be misleading. The alkalies, after they have done their work during the earlier stages of the calcination, being relatively volatile, are to a considerable extent driven off when extreme temperatures are reached, and they are found only in small quantities in well burned cements. We shall treat of this question hereafter when discussing the induration of cements.

CHAPTER II.

THE BURNING OF LIME.

CONTENTS.—Essential Conditions to be Observed—Common Kilns—Continuous or Shaft Kilns—Separation of the Fuel from the Lime Products—The Rüdersdorf Kiln—The Hoffmann Kiln.

Essential Conditions to be Observed.—It will be evident, from the study of the chemical facts contained in the foregoing chapter, that the preparation of lime, for the builder or the farmer, is a very simple operation, and the process of lime-burning, though an art of the highest antiquity, has not received the same amount of care and attention as that devoted to the manufacture of cements. The lime burner has merely to expel the carbonic acid, and he is not called upon to study the very complicated reactions involved in the production of cements.

Antiquated Form of Kiln.—The earliest lime kilns were probably merely pits or hollows sunk in the ground, or excavated in the face of a bank or hillside, in which the limestone or chalk could be raised by the heat of burning coal, peat, wood, or other fuel, to the temperature needed to expel the carbonic acid. These crude kilns were often lined with some refractory material—brick or stone—and, where fuel was costly, devices were introduced to drive the heat through a considerable depth of the raw material, for which purpose a conical hood or chimney was added, and the body of the kiln or “shaft” was lengthened. The first kilns were doubtless of the intermittent type—i.e., the kiln charged with the raw material was burnt out and allowed to cool. The lime was then drawn out, and a fresh charge of raw material was introduced, to be in turn converted into lime. This process, in which there is a great waste of heat, is still in common use in many parts of the country, but in some places the old-fashioned kiln has given place to the so-called “draw kiln,” or running kiln, in which the firing process is continuous, in order to effect which the total height of the kiln is greatly increased.

There is always, at the top of the draw kiln, a charge of raw materials, becoming gradually heated by the surplus heat from the calcination of the stone into lime, in the central or hot zone, beneath which the calcined stone is in turn getting slowly cooled down so as to permit of its extraction at the bottom of the shaft as burnt lime.

Forms of Continuous or Draw Kilns.—Kilns of this type may, it

is evident, be arranged as vertical shafts, or the heat may pass horizontally through a tunnel, one end of which is the firing end for the insertion of the raw stones and fuel, and the other end, nearest to the exhaust flue, or chimney, being used for the removal of the calcined material after being converted into lime. If a horizontally-fired kiln of this type is built in the form of a ring, we obtain the annular continuous kiln patented by Hoffmann; or if the kiln is a mere straight tunnel, with a moving charge, we have the plan patented by Bock.

Separation of the Fuel from the Lime Products.—In order to obtain the lime free from admixture with the ash of the fuel, and thus to secure a material which shall present a better appearance and command a higher price, various plans of firing have been practised. They all aim at conveying the heat into the lime from a separate fire-chamber. The well-known "flare kilns," in use in the south of England for burning the chalk lime, are familiar examples of this principle, and in these kilns the fuel is burnt on fire bars beneath the charge. In loading the kiln, which has to be done by hand, rough arches are formed out of some of the larger lumps of chalk, so as to serve as fire-chambers, the heat from which strikes upwards throughout the entire mass, gradually converting the whole kiln-charge into lime. All kilns of this type involve the use of a rather larger quantity of fuel than those where the fuel is interstratified or mingled with the raw material.

Shaft Kilns with Separate Fireplaces.—Even in the case of running kilns or draw kilns, it is quite possible to provide fire-chambers surrounding the hot zone of the kiln, in which the fuel is consumed free from actual contact with the stone, and the products of combustion pass from the fireplaces into the central shaft. In some cases the kilns constructed on this plan are of very large dimensions, and the firing is so arranged that the amount of heat lost is very small. It is, however, evident that a certain amount of heat must pass into the walls of the fire-chamber, and thus lead to a waste of fuel, although a well-designed continuous kiln, with outside fires suitably disposed, will produce a pure clean lime, free from ash, at a relatively small cost.

Advantage of Aqueous Vapour in the Kiln.—The fact ascertained by Gay-Lussac, and mentioned on page 3, that aqueous vapour may be made to play an important part in the expulsion of carbonic acid, should be remembered in connection with lime burning. In nearly all cases the stone or raw material contains naturally a large proportion of moisture, but in some forms of vertical kilns all the moisture is driven off in the upper part of the kiln, before the hot zone, which is in the vicinity of the furnace chambers, is reached, and in such cases the burning can be to some extent facilitated by the introduction of steam into the kiln along with the air needed for combustion.

Experienced burners often wet the stone before burning it, which is a rough and ready way of attaining this object.

Choice of Kilns for Limes of Different Kinds.—The choice of a suitable kiln for burning the limestone must, to some extent, depend upon the chemical composition of the raw material. Certain of the hydraulic shales of the lias series, the chalk marls of Cambridgeshire, and the clayey limestones of the coal measures, are liable, if the calcination is conducted at too high a temperature, to become partially fused, and in this condition to cake together and to obstruct the draught; or, in running kilns, to cling to the walls of the kiln, and thus render the downward movement of the contents no longer possible. It is manifest that limestones of this kind require very great care in burning, and would be difficult to calcine in shaft kilns, unless special arrangements were provided for access to the heated mass in the vicinity of the firing zone. A kiln which is admirably adapted for burning a pure chalk or a mountain limestone would no doubt prove quite unsuitable for the calcination of these more fusible substances, and its introduction for this purpose would probably prove a failure.

The Admixture with Ashes.—For many purposes for which lime is used commercially, it is very important that it should be as pure as possible, and free from the ash or clinker arising from the fuel. It is perhaps less essential now than was formerly the case that the lime used by the builder should be kept apart from the ash of the fuel, as in nearly all important works it is customary to prepare the mortar in a mill, which would crush up these substances along with the lump lime and incorporate them in the mortar. For the use of the plasterer, the lime is slaked and run through a sieve, by which means all the impurities and underburnt particles are eliminated. A much better looking lime no doubt results from the use of kilns in which all contact with the fuel is avoided; and although the cost of doing this adds, as we have seen, to the expense of the burning, it is certainly worth while to endeavour, if possible, to keep out the ash and clinker.

Continuous Shaft Kilns.—This fact has led to many recent inventions for kilns in which the lime is caused to pass down a shaft, and to be acted upon by furnaces or flames in the course of its progress. In nearly all of these kilns it becomes a matter of necessity to provide for a very considerable column of the material under treatment, because space is needed (a) for a charge of raw material to be dried and heated by the superabundant heat of the materials undergoing calcination in the hot part of the kiln; (b) for a stratum of limestone at the level of the furnaces, which must be maintained for some time at a dull red heat; and (c) for a space beneath the firing zone in which the lime can be cooled down sufficiently to permit of its removal at the lowest level. To

work a kiln of this type with the utmost economy, it has been found that a total height of from 30 to 50 feet is needed. It is not expedient to increase the internal diameter to more than from 7 to 8 feet, except in the case of a pure limestone; and where the height of the shaft exceeds 40 feet, the process does not answer well, except with hard stone. The danger in the use of lofty kilns is the risk of the formation of pipes or chimneys, through which the draught rushes upwards with great rapidity, leaving a considerable part of the charge either in a raw state or very imperfectly calcined. When the wind happens to be direct on to the draw-holes, screens or shutters are needed to moderate the draught, and unless in the hands of skilful and competent burners, lofty kilns are wasteful and unsatisfactory. In any case it will be found of advantage to provide for the admission of air all round the base of the kiln and at several different levels, and to enable the burner to control the air-inlets by means of shutters or dampers.

The Rüdersdorf Kiln.—All writers on limes have described the draw kilns of Rüdersdorf, which are typical of many of the Continental attempts to reduce the amount of fuel needed for calcination. The kilns at Rüdersdorf are polygonal (5- or 6-sided) on plan, and consist of a central shaft which is composed of double truncated cones joined at the bases, the diameters of which vary from 7 feet at the narrowest part, at the top or charging level, to 10 feet at the broadest part of the hot zone, just above the fire-chambers. From this level the kiln-shaft contracts as an inverted cone to the base, where the calcined lime is extracted about every ten or twelve hours, in quantities of some 50 cwts. at a time. The fire places, which are constructed in the thick hollow walls of the kiln, are five or six in number, and communicate with the kiln-shaft by arched openings. The total height of the shaft is about 40 feet, and it is about 10 feet from the base to the level of the fire-chambers. Arched passages surround the base of the kiln, and in them openings are provided through which to draw out the calcined lime. The thick walls of the kiln are carried up so as to form a level platform at the top, to which the stone is raised for charging purposes.

The proportion of fuel to burnt lime is set down at one to four. The fuel, which is very inferior coal, is burnt on firebrick perforated grates, and only the flame and products of combustion can enter the kiln-shaft. The ash falls into a pit beneath the fire-chambers, and is from time to time removed by special openings provided with shutters. In recent modifications of the Rüdersdorf kiln the fireplaces have given place to generators for producer-gas, and the shaft is provided with a cone or chimney like a Portland cement kiln, and the modern kilns are arranged for a much larger output, as much as 10 to 15 tons per diem in some cases. The coal consumption may range from 25 to 36 per cent. of the total output. The

drawing takes place at regular intervals. The kiln introduced by Fahnehjelm is the latest type of this mode of construction. It is fired by means of gas produced in a generator.

The Hoffmann kiln has been used with excellent results for lime burning, though of course in this case there is an unavoidable mixing of the ash of the fuel with the lime. The Dietzsch kiln is also employed for burning lime, and in many parts of the Continent it is usual to burn bricks and lime in the same kiln. Descriptions of the above kilns will be found in the chapter dealing with the calcination of cements.

CHAPTER III.

RETROSPECTIVE AND HISTORICAL REVIEW OF THE
CEMENT INDUSTRY.

CONTENTS.—Smeaton's Discoveries—Practical Experiments—Cause of Hydraulicity—Use of Trass and Puzzuolana—Composition of Mortars—Parker's Patents—Pasley's Tests—French and English Quick-setting Cements—Rosendale and American Natural Cements—Vicat's Artificial Lime—Frost's Patents—Early Cement Works.

Smeaton's Discoveries.—As we have stated in our opening chapter, the investigations of Smeaton undoubtedly paved the way for all the modern improvements in the treatment of limes and cements, and led to the overthrow of theories and prejudices which were as old as civilisation itself.

The discoveries of Smeaton, though they took place about 1756, were not published until many years later. In fact it was not until 1791 that he described his experiments, in the third chapter of Book IV. of his *Narrative of the Building, &c., of the Eddystone Lighthouse*.

Smeaton tells us that having been taught a simple method of analysis by Mr. Cookworthy (to whom, by-the-bye, we owe the first use of kaolin in this country, discovered by him in Cornwall and with which he subsequently produced the highly-prized porcelain of Plymouth and Bristol), he tested many varieties of lime, and soon found that the "acquisition of hardness under water did not depend upon the hardness of the stone (from which the lime was made), inasmuch as chalk lime appeared to be as good as that burnt from Plymouth marble, and that Aberthaw lime was greatly superior to either for aquatic buildings, though scarcely so hard as Plymouth marble."

Smeaton's Practical Experiments.—Till this point Smeaton had been guided by the experience of the past, for all writers on building, from Vitruvius to Belidor, had maintained this theory—viz., that lime burnt from dense hard stone made the hardest mortar. But Smeaton's practical tests upset all these traditions, and he sought for some better explanation. He goes on to say "I was very desirous to get some light into some of the sensible qualities that might probably occasion the difference, or at least be a mark of distinction." He then proceeds as follows:—

"Perhaps nothing will better show that the qualities of lime for water

mortar do not depend on hardness or colour than a comparison of the white lias of Somersetshire (which, though approaching to a flinty hardness, has yet a chalky appearance) with what is called near Lewes in Sussex the clunch lime; a kind of lime in great repute there for water works, and indeed deservedly so. This is no other than a species of chalk, not found like the lias in thin strata, but in thick masses as chalk generally is; it is considerably harder than common chalk, but yet of the lowest degree of what may be denominated a stony hardness; it is heavier than common chalk, and not near so white, inclining towards a yellowish ash colour. This stone when analysed is found to contain $\frac{3}{8}$ part of its weight of yellowish clay, with a small quantity of sand seemingly of the crystal kind, not quite transparent, but intermixed with red spots."

Hydraulicity Depends on Presence of Clay.—"Hence the fitness of lime for water building seems neither to depend upon the hardness of the stone, the thickness of the stratum, nor the bed or matrix in which it is found, nor merely on the quantity of clay it contains, but, in burning and falling down into a powder of a buff-coloured tinge, *and in containing a considerable quantity of clay*, I have found all the water limes to agree. Of this kind I esteem the lime from Dorking in Surrey to be; which is brought to London under the idea of its being burnt from a stone,* and in consequence of that, of its being stronger than the chalk lime in common use there; though in fact it is a chalk, and not much harder than common chalk, it contains $\frac{1}{7}$ part of light coloured clay of a yellowish tinge."

Colour not of Itself a Sufficient Indication.—"There is in Lancashire a lime famous for water building called Sutton lime; I have lately had an opportunity by favour of John Gilbert, Esq., to get a specimen of the stone in its natural state. I had long since seen it in the Duke of Bridgewater's works, both in the burnt stone and slaked, made up for use and in the water. I observed that it agreed with the lias in being of the buff cast. The stone itself is of a deep brown colour, and the piece I have is from a stratum about 3 inches thick, with a white clayey coat on each side. The goodness of the quality as water lime does not, therefore, consist in the colour before it is burnt; for we have already seen blue, whitish, and now brown, to be all good for that purpose, but they all agree in the colour or hue after they are burnt and quenched: and having analysed the Sutton limestone I find it to contain not only near $\frac{3}{8}$ part of the original weight of the stone, of brown or red clay, but also $\frac{1}{2}$ of fine brown sand, so that in reality I have seen no lime yet, proved to be good for water building, but what on examination of the stone contained clay: and though I am very far from laying this down as

* See Dorking Stone Lime, Appendix E.

an absolute criterion, yet *I have never found any limestone containing clay in a considerable quantity but what was good for water building*, and limes of this kind all agree in one more property, that of being of a dead frosted surface on breaking, without much appearance of shining particles."

Use of Trass and Puzzuolana.—In the same spirit of painstaking research Smeaton experimented with mixtures of lime with trass and puzzuolana, which substances were known at that day to impart to fat limes hydraulic properties. For reasons, which he explains, he rejected the former and employed a mixture of blue lias lime from Watchet and puzzuolana in equal parts, as this was, he conceived, the best water cement that could possibly be made. He likewise tried many other substances mixed with lime, such as the scales from a smith's forge and calcined iron ore.

The lime of Watchet, which he had found to be identical with that of Aberthaw (the beds being merely intersected by the estuary of the Severn), he caused to be slaked on the spot with just sufficient water to enable it to fall down to a fine powder, and this slaked lime was then packed in water-tight casks and sent to Plymouth, whence it was conveyed to the Eddystone rock for use as required.

The Varieties of Mortars used by Smeaton.—Smeaton gives an interesting table showing the composition of the various kinds of mortar he employed, as also the cost of each :—

No.	Name of the Mortar.	Winchester bushels by striken measure of			No. of cubic feet.	Expense per cubic foot.
		Slaked lime powder.	Puzzu- olana.	Common Sand.		
1	Eddystone mortar, . . .	2	2	...	2·32	s. d. 3 8
2	Stone mortar, . . .	2	1	1	2·68	2 1½
3	„ 2nd sort, . . .	2	1	2	3·57	1 7½
4	Face mortar, . . .	2	1	3	4·67	1 4
5	„ 2nd sort, . . .	2	½	3	4·17	1 1
6	Backing mortar, . . .	2	¼	3	4·04	0 11

Smeaton is said by General Pasley* in his well-known work, to which we shall often refer, to have been the first English engineer to use puzzuolana, which he read of in the works of Belidor, but for want of chemical knowledge Smeaton failed to appreciate the full significance of the facts that he had observed.

Parker's Patent in 1791.—Within a very few years of the publica-

* *Observations on Limes, Calcareous Cements, Mortars, Stuccos, and Concrete.* . . .
By C. W. Pasley, C.B. London, 1838. 8vo.

tion of Smeaton's work we find the record of Parker's invention of the cement made from "certain stones or argillaceous productions." His name, indeed, first appears in the "Patent Library Index" in 1791, when James Parker, of Christ Church, in the County of Surrey, claims, in Patent No. 1,806, the sole right to employ "a certain material never before made use of" for "burning bricks and tiles, and calcining chalk, earth, stone, and limestone." This he discloses in his specification to be "peat or bog," which was to be interstratified in the kiln with the material to be calcined. As an indication of the quantity needed, he states: "as, for instance, if it requires 36 bushels of coal to burn 220 bushels of lime, the same may be burnt or calcined with 220 bushels of peat with the addition of 3 bushels of coals."

Parker's Second Patent for Cement.—We cannot say with certainty, though it seems probable, that this was the same James Parker who on 28th June, 1796, claims, in Patent No. 2,120, the invention of "A certain Cement or Terras [trass] to be Used in Aquatic and other Buildings, and Stucco Work." He describes his process as follows:—"The principle and nature of the said Invention consists in reducing to powder certain stones or argillaceous productions, called noddles (*sic*) of clay, and using that powder with water so as to form a water (mortar?) or cement stronger and harder than any mortar or cement now prepared by artificial means. I do not know of any precise generical term for these noddles of clay; but I mean by them certain stones of clay or concretions of clay, containing veins of calcareous matter, having frequently but not always water in the centre, the cavity of which is covered with small crystals of the above calcareous matter, and the noddles agreeing very nearly in colour with the colour of the bed of clay in or near which they are found. These noddles, on being burnt with a heat stronger than that used for burning lime, generally assume a brown appearance and are a little softened, and when so burnt and softened become warm (but do not slack) by having water thrown upon them, and being reduced to powder after burning, and being mixed with water just sufficient to make them into a paste, become indurated in water in the space of an hour, or thereabouts. Any argillaceous stone, then, corresponding with this description, whether known by the name of noddles of clay, or any other name, is the sort and kind only that I mean to appropriate to my own use in the fermentation (formation?) of my cement."

The Preparation of the Cement.—"The manner in which I prepare and compose this cement is as follows, viz.:—The stones of clay or noddles of clay are first broken into small fragments, then burnt in a kiln or furnace (as lime is commonly burnt) with a heat nearly sufficient to vitrify them, then reduced to a powder by any mechan-

ical or other operation, and the powder so obtained is the basis of the cement."

Mode of Using the Cement.—"To compose the cement in the best and most advantageous manner, I take two measures of water and five measures of the powder thus described; then I add the powder to the water, or the water to the powder, taking care to stir and beat them during the whole time of intermixture; the cement is then made, and will set or become indurated either in ten or twenty minutes after the operation has ceased, either in or out of water.

"But although I have described what I consider as the best proportions for the composition of the cement, it is expressly to be understood that these and all other proportions are to be included within the meaning and purpose of this specification, but that no other proportions will produce so strong a cement in so short a time as those I have here pointed out; and also that I occasionally burn, and grind, and mix the powder before described with lime and stones, clay, sand, or calcined earth in such proportions as may be necessary and useful for the purpose that the cement is intended to be applied to, always observing the less water is used the better, and the sooner the mortar or cement is used after being made the stronger and the more durable it will be."

Parker's Cement termed Roman Cement.—In the above patent Parker is described as of "Northfleet, in the County of Kent, gentleman." According to Pasley it was not until some years later that he applied to the new material the misleading name of "Roman" cement. He shortly afterwards traded in partnership with Mr. Wyatt, and used the stones found at Sheppey in the manufacture of the cement, which soon became widely known under the name of "Parker's cement." A certain Mr. Samuel Wyatt had previously acquired experience in the use of materials for stucco, and his name is frequently mentioned by Dr. Higgins in his work on Cements.*

Derivation of the Septaria.—The "pebbles" used for cement making were obtained at various places on the Kentish coast, those from Minster Manor and Whitstable being apparently in the best repute. It was not until very much later that Frost made use of the Harwich dredged stone, after which time it was customary to employ a mixture of Harwich and Sheppey stones in equal proportions to produce the best Roman cement, though Pasley tells us that about 1836, in the Government dockyard at Sheerness, they used one part of Sheppey to three parts of Harwich cement stone. The makers of artificial cements about this period sold

* *Experiments and Observations made with the view of improving the art of Composing and applying Calcareous Cements, . . .* by Brindley Higgins, M.D. London, 1780. 8vo.

the cement made from natural stone at a much higher price than that made from a mixture of chalk and clay.

Pasley's Tests of Cements in 1836.—The following table compiled from Pasley's book is valuable as showing the comparative merits of the chief cements in use at the time he wrote [1836]. All the specimens were tested neat:—

Sort of Cement used.	Age in Days.	Total Tensile Strength in Pounds.	Strength in Lbs. per Sq. in.
Pasley's artificial cement, .	11	1,395	34·9
Frost's „ „ .	11	705	17·6
Francis (Natural), „ .	11	1,223	30·6
Sheerness „ „ .	{ 10 12 }	1,220	30·5

French Quick-Setting Cements.—The quick-setting cements of the Roman type, made in accordance with Parker's patent, had their counterpart in France, for about 1796 a French military engineer, named Lesage, drew attention to the eminently hydraulic properties of the pebbles of Boulogne-sur-Mer, and from these he produced a material which he called "plaster-cement," though this substance was quite distinct from the compounds of the calcium sulphate series.

Another quick-setting cement, which obtained a wide reputation on the Continent, was that of Pouilly, discovered by Mons. Lacordaire in 1829. Four years later, in 1831, Mons. H. Gariel first introduced the well-known cement of Vassy. Another cement of a similar character, which has been much used in France, is made from stone dug near Grenoble at Porte-de-France.

Analyses of French and English Cements.—The composition of all these materials is very similar, as will be seen by the following set of analyses, made in Paris, at the École des Mines:—

	English Roman Cement.	Boulogne Cement.	Cement of Vassy.	Cement of Pouilly.
Silica,	15·42	14·27	16·0	17·14
Alumina,	5·63	5·81	6·50	6·87
Iron oxide,	6·81	5·97	8·60	4·83
Magnesia,	0·83	0·67	1·50	3·39
Manganese,	0·54	0·83	...	0·17
Lime,	45·12	46·20	46·80	47·35
Loss on calcination; moisture, and carbonic acid,	25·65	26·25	20·60	20·25
	100·00	100·00	100·00	100·00

The Vassy cement, which is very dark in colour, is the richest in iron oxide, and sets when freshly burned with great rapidity. The cement of Grenoble is very similar in its composition to the above, but contains rather less clay. In France, the quick-setting cements are, as a rule, ground under edge-runners, and passed through copper wire sieves of 324 meshes per square centimetre (2,090 per square inch). The average specific gravity of these cements varies from 0.96 to 1.10.

Magnesium Cements of America.—Of the so-called natural cements of America, which, before the introduction of the manufacture of Portland cement, had obtained such a wide-spread employment in every kind of engineering work in that country, many partake somewhat of the nature of Roman cement, and may be mainly considered, according to one of the most recent American writers on this subject—Cummings*—under two heads, as double silicates, or triple silicates. The former class includes all rock cements composed of bisilicates of lime and alumina, and the latter the trisilicates of lime, magnesia, and alumina. It is stated that in 1894 the annual production of American rock cements amounted to 7,595,676 barrels, and the proportions of these two classes were as follows:—

1. Bisilicates, - - - -	2,557,464 barrels.
2. Trisilicates, - - - -	5,038,212 „

It must be understood that the above classification is somewhat arbitrary, as many of the so-called bisilicates will be found to include a small percentage of triple and also of a single silicate. The position of a cement in the above classification depends therefore on the particular form of silicates indicated by its predominance. The bisilicates are, as a rule, of the Portland cement type, and are frequently calcined at a white heat; the trisilicates are fired at a lower temperature, and are more of the nature of Roman cement. As a type of the trisilicate cements, we may describe the famous Rosendale cement, named after the town of Rosendale, where it was originally discovered, and largely used in the construction of the old Delaware and Hudson canal.

Raw Materials for American Cements.—The formation which furnishes the raw materials for this cement is an argillaceous magnesian limestone, which extends along the whole of the Appalachian range, and was said to yield formerly three-fourths of the hydraulic cement produced in the United States. The workable beds are seventeen in number, and the method of manufacture is as follows:—

The limestone, which is blasted by black powder, is conveyed to the kilns on trucks running along the base of the quarry. The stone is arranged in the kilns in layers interstratified with small coal. The kilns are cylindrical in form, but have a conical contraction at the bottom.

* *American Cements*, by Uriah Cummings. Boston, 1898.

They are worked continuously, portions of the charge being withdrawn every twelve hours. The underburnt lumps are passed a second time through the kiln; the fully calcined stone is conveyed in elevators to the top of the mill. Here it is first broken to a small gauge (size of hazelnut) in a cracker, which is a machine somewhat on the principle of the coffee-mill. Each cracker will prepare from 250 to 300 barrels of cement *per diem* for the mills.*

Grinding of the Calcined Cement.—The mill-stones are only 3 feet in diameter, but they grind the cement so fine that from 93 to 95 per cent. will pass a 50 × 50 mesh sieve. These mills differ from those in use in this country for cement-grinding, in that what is termed in England the “runner” or the upper stone is fixed and the lower one revolves. The ground cement is conveyed by “creepers” to the packing room, where it is put up in paper-lined casks and is then ready for use.

Yield and Composition of the Beds.—Each cubic yard of cement stone yields about 2,700 lbs. of finished cement. The various beds of stone fluctuate very considerably in their composition, and the preparation of the cement and the mixture of the raw materials from the different levels is a matter of great nicety. During the manufacture the cement is carefully tested; four briquettes being made every hour. The pattern used for the moulds differs from that in common use in Europe.

General Gillmore's Tests.—General Gillmore, whose work on cements* may be consulted with advantage respecting the manufacture and employment of these materials, puts the crushing strength of the neat cement at 546 lbs. per square inch in seven days, and 2,015 lbs. per square inch in thirty days. The tensile strength of the neat cement is 104 lbs. per square inch in seven days, and 134 lbs. per square inch in thirty days. With an equal amount of sand the tensile strength in thirty days is 102 lbs. per square inch.

Louisville Cement.—Cement rock was discovered at Louisville, Kentucky, in the year 1829, and, having been used for the Louisville and Portland Canal, it was found to be of good quality. This district, owing to the convenience of transport afforded by the Ohio River, speedily became the centre of an important industry, second only to that of the Rosendale district. The Louisville cement contains less magnesia than the Rosendale, for while the magnesia in the former may average from 9 to 10 per cent. the magnesia found in the Rosendale cement may reach as much as 18 per cent. The stone from which the cement is made is peculiar to a small area, only a few miles wide, extending north of the Ohio River about 15 miles. No admixture of various strata is necessary

* *Practical Treatise on Limes, Hydraulic Cements, and Mortars*, by Q. A. Gillmore, A.M. New York, 1874.

in making this cement, the formation being uniform in all essential characteristics. The stone, much of which is mined in open quarries, is broken into pieces of three uniform sizes by crushers and fed into the kilns, which are 45 feet high and 16 feet in diameter. These kilns are constructed of iron, lined with firebrick; the stone is burnt with coal loaded into the kiln in alternate layers with the stone. The firing operations are continuous, and the kilns, which are lighted in the spring, are only extinguished when the operations cease for the winter. The calcined stone is withdrawn from openings near the base of the kiln and fed into the coarse crushers, and all imperfectly burned material is picked out by hand. From the coarse crushers the stone passes into the fine crushers, and it is ultimately ground to powder between emery mill-stones.

Extensive works for the production of rock cement exist also at Milwaukee, Buffalo, La Salle, Utica, Akron, at various parts of the Lehigh Valley, and in Georgia.

While certain of the rock cements are calcined at a relatively low temperature, others are burnt at a heat which approaches that required to produce Portland cement clinker, and the colour varies between very wide limits.

Natural Cements now held in less esteem in America.—Owing to the great impetus given in recent years to the manufacture of Portland cement in the United States, the production of natural cements would appear to have fallen off. We have dealt with the analysis of the American natural cements at p. 53.

Early Cement Patents in England.—The records of the Patent Office of this country show us that prior to the advent of Parker some eighteen inventors had busied themselves with processes for burning lime, for the manufacture of "tarrass" or puzzuolana, for a composition or cement called "Pietra Cotta," and for sundry descriptions of mastic, mortar, and stucco. Among these we find the "water cement or stucco" described in the work already mentioned of Dr. B. Higgins. This patent is No. 1,207, and is dated Jan. 8, 1777.

From the date of Parker's second patent in 1796 to that of James Frost's specification in 1822, the Patent Index likewise includes eighteen patents, one of the most notable of which was that granted to St. Leger in 1818.

St. Leger's Patent in 1818.—St. Leger was probably the concessionaire of Vicat, a French engineer, whose experiments with limes and cements are justly famous, and his work may here receive passing notice. Omitting the investigations of Lorient, published in 1774, of De La Faye, said to have been made known in 1777, and the artificial stone of Fleuret, described in his book dated 1807, all of which are duly recorded by

Pasley, we come to the publication of Vicat in 1818.* It will be impossible here to do more than refer most briefly to his treatise, but as his later work in 1828† has been ably translated by Captain Smith, and as General Pasley alludes at considerable length to his investigations in the appendix to his "Observations on Lime, Calcareous Cements, &c.," we need not dwell on them very fully.

Vicat's Artificial Lime.—Vicat, who appears to have been the first to apply the term "hydraulic" to limes for use in water, prepared mixtures of pure lime and clay, and calcined the resulting material in kilns. He employed, originally, slaked lime powder together with 20 per cent. of clay, but in his second treatise he describes a plan of grinding chalk along with the requisite proportion of clay. His process was actually carried out at Meudon by Messrs. Bryan and St. Leger, who used the chalk found in the vicinity, and the plastic clay of Vaugirard. They ground together in a washmill four measures of chalk and one of clay with a considerable quantity of water, and the fluid slip was then run into reservoirs to dry. When stiff enough the pasty mass was moulded into blocks and burnt in kilns, interstratified with small coal and coke. This plan of making an artificial lime was still practised at Meudon when one of the authors visited the works in 1878.

Vicat shares with Dr. John of Berlin the honour of having explained the importance of the presence of clay in combination with lime on scientific grounds, though De Saussure first pointed out that hydraulicity depended solely on the presence of clay, and Descotils in 1813 observed that this phenomenon was due to the existence of a large quantity of siliceous matter disseminated through the mass in very fine particles. Dr. John's treatise was published in 1818. Smeaton, as we have stated, anticipated by many years these discoveries, though he failed to turn them to practical account.

Specification of St. Leger's Patent.—Doubtless it was a process similar to the above which was, as we have seen, patented in this country in 1818 (No. 4,262). M. Maurice St. Leger describes himself in the specification as of St. Giles, Camberwell, in the County of Surrey. The patent is for "an improved method of making lime" out of a fat or pure carbonate of lime by the addition to the same of "clay or any substance containing alumine and silex." The general proportion named by St. Leger is "from 1 to 20 measures, or given quantities of clay or other substance containing alumine and silex, to every 100 measures or given

* *Recherches Expérimentales sur les Chaux de Construction, les Bétons et les Mortiers Ordinaires*, par L. J. Vicat. Paris, 1818. 4to.

† *Résumé des connaissances positives actuelles sur les qualités, les choix et la convenance réciproque des matériaux propres à la fabrication des Mortiers et Ciments Calcaires*, &c., par L. J. Vicat. Paris, 1828.

quantities of chalk, stone, or other substance, or of lime." It does not appear that St. Leger worked the patent in England.

Frost's Patent for British Cement in 1822.—On the 11th of June, 1822 (No. 4,679), James Frost, of Finchley, in the County of Middlesex, Builder, specifies "a new cement or artificial stone," which is made as follows:—"I select such limestones or marls, or magnesian limestones or marls as are entirely or nearly free from any mixture of alumina or argillaceous earth, and contain from 9 to 40 per cent. of siliceous earth or silica, or combinations of silica and oxides of iron, the silica being in excess and in a finely-divided state, and break such selected materials into small pieces, which are then calcined in a kiln, in the manner calcareous substances usually are, until all carbonic acid be expelled, and until it be found on trial of a small portion of such calcined materials that it will not, when cool, slack or fall when wetted with water. The calcined material is to be ground to a fine powder by any machinery fit for reducing dry substances to that state, and the powder is the material for making the cement or artificial stone, and must be kept in dry packages for use. When used it is to be mixed with water, and tempered to the consistency of common mortar; it should be mixed in small quantities and applied instantly to its intended purpose, as it will set in a few minutes to resist the impression of the finger and gradually harden to a stony body. For many purposes a quantity of clean siliceous sand may be advantageously incorporated with it when it is tempered for use. The cement will be lighter or darker in colour, as there is a lesser or greater quantity of oxide of iron in the selected materials; the lighter colour will be found best adapted to dry, and the darker colour to wet situations.

"I declare that my invention is for making a cement or artificial stone from siliceous limestones or marls in the manner hereinbefore described, and that I shall call it by the name of British cement."

There are some singular blunders in this specification which prove conclusively that Frost had a poor grasp of the subject. Thus he proposes to use limestone or marl "free from any mixture of alumina," but containing "from 9 to 40 per cent. of silica," which would be simply sand, and would inevitably yield a compound devoid of cementitious properties.

Frost's Second Patent.—In 1823 (No. 4,772), Mr. Frost describes a process of "calcining and preparing calcarious (*sic*) and other substances for the purpose of forming cements," with which object he used a kiln of special construction, in which the material was permitted to cool very slowly; this is an invention of no importance, and it was probably founded on a misconception.

Frost as a Cement Maker.—Very shortly afterwards, in 1825,

Frost established himself in cement works at Swanscombe, on the Thames, and became the first maker of artificial cement in the London district. Frost's business was carried on by him until 1832 or 1833, when his interest was acquired by Mr. John Bazley White, Senr., who at first was the partner of Mr. Francis. Pasley tells us that Messrs. Francis, White & Francis "were in the habit of selling their artificial cement at one shilling per bushel at the same time that they sold their natural cement for eighteenpence."

Mr. Frost, when he had disposed of his business, retired to America, and we can find no further records of his career. His works were carried on by Messrs. Francis & White in partnership until January 1st, 1837, when they were made over entirely to Messrs. White & Son, who had also works at Millbank. Mr. Francis, who traded as Messrs. Francis & Sons, founded the well-known works at Nine Elms, Vauxhall.

In strict historical sequence we should before this have referred to Aspdin and his invention of Portland cement, but this may form the subject of a special chapter.

CHAPTER IV.

THE EARLY DAYS OF PORTLAND CEMENT.

CONTENTS.—Portland Cement first made by Aspdin—His Specification for Cement—Cements made from Artificial Mixtures—Roman and Quick-Setting Cements—Pasley's Experiments—Becker's Account of Portland Cement—J. M. Maude, Son & Company's Circular—Early Tests of Portland Cement—Use of Portland Cement in Thames Tunnel—Aspdin's Circular—Experiments at Exhibition of 1851—Johnson's Experiments.

Portland Cement first made by Aspdin.—The somewhat misleading name of "Portland" cement was given to the artificial compound of lime and clay, prepared by Mr. Joseph Aspdin, a Leeds bricklayer. He chose this name in consequence of its fancied resemblance in point of colour and texture to the oolitic limestone of the island of Portland, well known and in great favour in this country as a building stone.

Aspdin's Specification.—Aspdin's specification, No. 5,022, is dated October 21st, 1824, and is for "An Improvement in the Modes of Producing an Artificial Stone," which invention he thus describes:—"My method of making a cement or artificial stone for stuccoing buildings, water works, cisterns, or any other purpose to which it may be applicable (and which I call Portland cement) is as follows:—I take a specific quantity of limestone, such as that generally used for making or repairing roads, after it is reduced to a puddle or powder; but if I cannot procure a sufficient quantity of the above from the roads, I obtain the limestone itself and I cause the puddle or powder, or the limestone as the case may be, to be calcined. I then take a specific quantity of argillaceous earth or clay, and mix them with water to a state approaching impalpability, either by manual (*sic*) labour or machinery. After this proceeding I put the above mixture into a slip pan for evaporation, either by the heat of the sun or by submitting it to the action of fire or steam conveyed in flues or pipes under or near the pan, until the water is entirely evaporated. Then I break the said mixture into suitable lumps, and calcine them in a furnace similar to a lime kiln till the carbonic acid is entirely expelled. The mixture so calcined is to be ground, beat, or rolled to a fine powder, and is then in a fit state for making cement or artificial stone. This powder is to be mixed with a sufficient quantity of water to bring it into the consistency of mortar, and thus applied to the purposes wanted."

Aspdin's Second Patent.—Aspdin, whose name, by-the-bye, in the "Alphabetical Index of Patentees" is misspelled "Apsdin," obtained protection in the following year, 1825, under date of June 7th (No. 5,180), for "a Method of Making Lime." In order to effect this, he collected the road scrapings from roads repaired with limestone; these he dried, either by natural or artificial heat, and they were subsequently "removed to a furnace or kiln to burn with coal, coke, or wood." The product was then ready either for "building, or liming land."

Aspdin's Process differs from that used subsequently.—It is difficult to recognise in this description a process likely to result in the formation of a cement of the present Portland type. It must be remembered, however, that Aspdin had a hard mountain limestone to deal with, and that probably the most easy way to obtain this material in a state of fine subdivision, in order to mix it with the clay, was to calcine it. It could then readily be slaked and reduced to powder. The next step was to temper it with the requisite amount of clay, and finally the mixture was submitted to a second process of calcination. This double-kilning would, where fuel was relatively cheap, entail but little more cost and perhaps less labour than first grinding the limestone to fine powder under mill-stones and then mixing it with the clay, as is now done in the dry process of manufacturing Portland cement. Moreover, by the slaking action, the lime is obtained in an extremely fine state of subdivision, and therefore in a condition peculiarly well adapted for intimate admixture with the clay.

Defects in Aspdin's Specification.—Aspdin fails to point out the exact amount of clay needed—rather an important matter in a specification, one would think—and he omits to state that the firing must be carried on until incipient vitrification is attained. These omissions might by some be regarded as casting doubts upon the authenticity of his discovery of Portland cement in 1824, but it is a well-known fact that he had a manufactory of Portland cement for many years at Wakefield which was established in 1825, and which is still in existence though no longer on the original site. Moreover, his son, William Aspdin, was, as we shall see, one of the early cement manufacturers in the Thames district.

Proposals to make Cements from Artificial Mixtures.—On searching the Patent Office records it is found (as we have already mentioned) that other inventors had attempted to produce cements from mixtures of lime and clay, and Pasley has, in his important work on cements, previously noticed, recorded a long series of patient investigations and experiments, having for their object the formation of an artificial cement capable of giving like results to those obtained from the natural cements, made from the septaria of the London

clay, and the nodules of argillaceous limestones found in the Isle of Sheppey.

Roman and Quick-setting Cements.—In our previous chapter we have given a brief account of these materials, and of the artificial hydraulic lime of Meudon, the invention of Vicat. Cements of this type were, in the early years of the nineteenth century, in very general use in this country, and many attempts were made by inventors to obtain a cheaper source of supply. It was clearly the search after such substitutes for the natural cement stone which led to the discovery of Portland cement, and though this latter material has now very largely displaced the quick-setting cements of former days, there are no doubt many purposes for which Roman cement can be used with advantage, and this cement is still in frequent demand.

Early History of Portland Cement by Pasley.—We know but little of the early history of Portland cement. General Pasley, in the preface of the second edition of his work, dated August, 1847, states:—"At present there are three manufactories of artificial cements in England, which have all been used more or less extensively in works of importance, and have given satisfaction, viz.:—First, that of Messrs. John B. White & Sons, in the Parish of Swanscombe, Kent, the present proprietors of Mr. Frost's Works, who, after gradually relinquishing the objectionable parts of his process, have succeeded in making a good artificial cement, which they call their Portland cement, by a mixture of chalk found on their own premises with the blue clay of the Medway; secondly, that of Messrs. Evans & Nicholson, of Manchester, who make an artificial cement, which has been called the patent lithic cement, with the very same ingredients, and in the same proportions, nearly, that were used in the author's experiments, but the most important of which is obtained in a roundabout manner from the residual matters or waste of certain chemical works, instead of working with natural substances; thirdly, that of Mr. Richard Greaves, of Stratford-upon-Avon, who makes a powerful water cement, which he calls blue lias cement, by mixing a proportion of indurated clay or shale with the excellent blue lias lime of that neighbourhood, both of which are found in the same quarries; the former being previously broken and ground, and the latter burned and slaked, which is absolutely necessary in making an artificial cement from any of the hard limestones."

Pasley's Letter to Dr. Garthe.—This account of the Portland cement industry was, however, incorrect, for we find in a letter published in Dingler's *Polytechnisches Journal*,* written by Pasley to Dr. Garthe of Cologne, and dated March 3rd, 1852, the following additional information on the subject:—"I am much flattered by the favourable opinion you

* Vol. cxxiv., p. 27.

express concerning my work on cement. As shortly after my promotion to the rank of Major-General I ceased to occupy the post of Inspector of the Royal Engineers' School at Chatham, and had, therefore, neither assistants, materials, nor appliances at my disposal, I was no longer in the position to prosecute researches of a similar nature to those formerly carried on by me, and which resulted in the discovery of an artificial compound but little inferior to the best natural cements.

"For several years past I paid no further attention to the subject until I learned that Portland cement was superior to Roman cement; and as it is the fashion in our country to disguise everything with some fantastic name or other, which, except in the case of chemical products, gives not the slightest clue to the composition of the article in question, I was astonished to discover that this Portland cement, the name of which would lead the foreigners visiting our great Industrial Exhibition of last year to believe very naturally, either that it was a cement found in the island of Portland, or that it was related in some way or other to Portland stone, was neither more nor less than my own artificial cement, compounded of chalk and clay.

"Messrs. Robins, Aspdin & Company manufacture Portland cement which appears to me to be just as good as, if not superior to, that of Messrs. White & Sons, although I never heard of it until I met Mr. Aspdin in the great Exhibition last year. I was present at all the experiments upon Portland cement mentioned in *The Builder* of the 27th September last. The results of the same are correctly reported, but several of them are rendered ambiguous for want of more complete particulars or of the explanatory drawings relating to them."

Becker's Book on Portland Cement in 1853.—In a German work on Portland cement by Becker,* in which this letter is quoted, and which, we believe, was the first treatise in any language on this material, there is a footnote calling attention to the singular fact that "although Joseph Aspdin, the inventor and patentee of Portland cement, established his manufactory at Wakefield in 1825, and his son, William Aspdin, founded his works at Northfleet, on the Thames, about 10 miles from Chatham, a few years later, at which latter place Sir C. W. Pasley was then residing, and although their Portland cement was already much employed on the Continent, as introduced in the first instance by Maude & Son, and subsequently by Robins, Aspdin & Company, whereas the cement of Messrs. White & Sons was not brought into the market until many years later (in 1845), Sir Charles Pasley only heard for the first time of the existence of Joseph Aspdin, the inventor of Portland cement, and of his manufactory [at Wakefield] in the great Exhibition of 1851."

Aspdin, the Younger.—Mr. Becker is, however, not quite correct

* *Erfahrungen über den Portland Cement*, Berlin, 1853. 8vo.

in his facts, for young Aspdin did not go to Northfleet until 1848. It appears that he at first associated himself with Messrs. J. M. Maude, Son & Company, of Upper Ordnance Wharf, Rotherhithe, and from a circular issued by this firm in 1843 we learn the following particulars respecting their business, and relative to the cement industry at that date:—

Circular by J. M. Maude, Son & Company.—"The manufacture of this cement (patent Portland cement) has for many years been carried on by Mr. Aspdin at Wakefield, in which neighbourhood, as throughout the northern counties of England, it has been successfully and extensively used; owing to the heavy charges attending its conveyance to the London market its consumption there has necessarily been limited, and although its superiority over other cements has never been contested by those who have been induced to give it a trial, the high price at which alone it could be supplied has hitherto proved a serious impediment to its more general introduction into the metropolis. Messrs. J. M. Maude, Son & Company have now the satisfaction of announcing to the public that they have made arrangements with the son of the patentee for the purpose of carrying on the manufacture of this valuable cement at their extensive premises at Rotherhithe; and whilst they will thus be enabled to supply it at a considerably reduced price, they have also the satisfaction of stating that in consequence of improvements introduced in the manufacture, it will be found, for the following reasons, infinitely superior to any cement that has hitherto been offered to the public:—

"(1) Its colour so closely resembles that of the stone from which it derives its name as scarcely to be distinguishable from it.

"(2) It requires neither painting nor colouring, is not subject to atmospheric influences, and will not, like other cements, vegetate, oxydate, or turn green, but will retain its original colour of Portland stone in all seasons and in all climates.

"(3) It is stronger in its cementitive qualities, harder, more durable, and will take more sand than any other cement now used."

After alluding to its value as a stucco and for paving purposes, the circular states—"It is manufactured of two qualities, and sold in casks of 5 bushels, each weighing about $4\frac{1}{2}$ cwts.—No. 1 at 3s. per bushel, or 20s. per cask, and No. 2 at 2s. 3d. per bushel, or 16s. 3d. per cask. 4s. 6d. each allowed for the casks, if returned in good condition." From the directions for its use we learn that the best quality was to be employed with four parts of sand.

Early Tests of Portland Cement.—Certain particulars are likewise given of some comparative trials of this Portland cement with Roman cement, which were conducted by Messrs. Grissell & Peto at the new Houses of Parliament in 1843, together with a letter from these eminent contractors, dated from York Road, Lambeth, 13th November, 1843,

setting forth the fact that the experiments in question, which consisted of bricks stuck one on to another projecting from a wall, and of brick beams with bearings of 3 and of 5 feet, were made by their direction and under their own superintendence, and they add—"The results as shown by the above statement afford very satisfactory evidence of the superior qualities of your cement." They conclude that Portland with three parts of sand was more than double the strength of Roman cement with one part of sand, and that with Roman at 1s. 4d. and Portland at 2s. 3d. the bushel there was a saving of from 1½d. to 2d. per bushel of mortar in using Portland, owing to the increased volume of sand this latter cement would carry.

Wylson on Portland Cement.—It was just about this period that Portland began to make a London reputation, and in some articles on "Mortars and Cements" in *The Builder* in 1844, Mr. Wylson, speaking of these same experiments, says: "The deductions thence arrived at show an advantage on the side of the Portland cement, which speaks most strongly in its favour; and which, judging by the authority from which these contrasts emanate, must be considered as at once authentic and conclusive, establishing this to be beyond all doubt superior to the Roman cement, whether as to strength, adhesion, or the capacity of receiving sand; the latter of which properties it is shown to possess to such a degree as to render it actually cheaper than the Roman cement, whilst its other recommendations of beauty and the saving of colouring alone render it highly preferable."

Early Advertisements relating to Portland Cement.—Advertisements relating to this cement as made by Messrs. J. B. White & Sons appear for the first time in *The Builder* in October, 1845, and on the occasion of an accident to some stucco on a house in Cornhill, which had failed or "blown," in the following year, Messrs. Maude, Jones & Aspdin write under date of 3rd September, 1846, to deny that the cement in question was of their manufacture.

Sir William Tite on Portland Cement.—In May of this same year, Mr. W. Tite, the then Vice-President of the Institute of British Architects, spoke of Portland cement as "a good material if properly made and properly applied."

We have now reached the period when the railway fever set in, and the demand for cement stone at Harwich became very extensive, indeed the stock of stone threatened to become exhausted. We read in December, 1846, "prices have in consequence risen 30 per cent., while the dredgers are reaping a proportionate benefit. It is calculated that £25,000 per annum are paid away in wages alone to workmen employed in this trade."

Predicted Exhaustion of Natural Cement Stone.—It must have been in the year 1845 or 1846 that Sir R. Peel announced in Parliament

his intention of taxing the cement stone, fearing its exhaustion, and hoping thus to reserve a sufficient supply for the purpose of Government works. This fact we learn from a pamphlet issued by Messrs. Aspdin, Ord & Co. about 1854, who state also therein that—"As soon as Mr. Wm. Aspdin heard of this he addressed Sir Robert Peel upon the subject, and intimated to him that he need not be alarmed about the supply of 'Roman cement,' as an article, which far surpassed it, was extensively manufactured. To prove these remarks, Mr. Aspdin waited upon Sir R. Peel with samples, and obtained a reply to the effect that he was much satisfied with them, and with the explanation; and in consequence the proposed tax was abandoned." In this pamphlet, which describes the firm as carrying on business at New Wharf, Abingdon Street, Westminster, and at Gateshead-on-Tyne, it is stated that their total manufacturing powers were equal to 3,000 casks per week, and the price of the cement is quoted at 2s. per bushel. The results are given of several series of tests, and there is a challenge to rival manufacturers, dated December 16th, 1852, to submit their cements to public test; in accordance with which, experiments were carried out at their wharf at Millbank on February 10th, 1853.

Portland Cement from Wakefield used in Thames Tunnel.—

From this same pamphlet we find that the Wakefield cement was largely used in the Thames Tunnel about 1828, although "at that time it cost 20s. to 22s. per cask, besides the carriage to London. Yet Sir I. Brunel decided (notwithstanding his ability to procure Roman at 12s. per cask delivered on the spot) to adopt Portland chiefly for his purpose, as its merits required no other recommendation than an impartial trial."

From this statement we may assume that the Thames Tunnel was the first engineering work of importance in which Portland cement was used, for there can be no doubt that in its early days it was mainly a stucco cement, and it was not until very much later that it acquired the confidence of the engineering profession.

Accident at Euston Station in 1848.—The year 1848 was in many ways a very eventful one in the history of Portland cement. On the last day of January a fatal accident occurred at Euston Station owing to the incautious use of Roman cement. A lofty wall supported on columns formed of brick on edge suddenly fell, causing the death of two workmen, and at the inquest which followed, and which attracted much attention, the question of the employment of cement was discussed at great length. Mr. Hardwick, the architect, expressed an opinion that the failure of the cement was due to its employment during the cold winter weather, and also to the great haste with which the work was run up. The columns in question were 20 feet high, 2 feet 2½ inches in diameter at the base, and 1 foot 10½ inches in diameter below the capital. Messrs. W. Cubitt

& Company, the builders, stated that they could not assign a reason for the fall of the wall. On February 11th, Mr. William Aspdin wrote from Northfleet and attributed the accident solely to the use of defective cement. We have here an intimation of Aspdin's removal from Rotherhithe.

Experiments at Messrs. Grissell's Works in 1847.—Later on in this same year, the results of some trials of Messrs. White's Portland cement are published in *The Builder*. These experiments had taken place at Messrs. Grissell's ironworks on December 10th and 31st, 1847, and they furnished additional evidence of the superiority of Portland over Roman cement.

Aspdin's Circular in 1848.—The above trials and the publicity they obtained seem to have given considerable umbrage to Aspdin and his partners, for in the September following he published a letter as an advertisement in *The Builder*, in which he set forth, among other matters, that this cement was first introduced by his father in 1813, and patented by him as "The Portland Cement" in 1824, and that the original material is solely made by him. He quotes certain tests to show that he had obtained far better results than Messrs. White had done, and that he had used more sand. Thus he states that he has made blocks consisting of one part of cement to ten parts of sand, and he concludes by calling attention to a public trial of their cement which the firm were about to institute at their wharf at Great Scotland Yard.

Experiments in 1848 at Messrs. Bramah's Works.—These proposed experiments they advertised for some time, and they challenged all other cement makers to compete with them. The trials came off on the 18th September, and subsequently at Messrs. Bramah's works on the 26th, when some blocks were crushed by hydraulic pressure. We extract the following particulars from *The Builder* of September 30th, 1848, as they show the quality of the cement at that period. The brick tests were of the usual character—viz., built out from the wall. In one case the beam consisted of 38 bricks with neat cement. With one part sand 15 bricks. Some brick beams were also tested, but the results are not very clear. Two large blocks of Portland stone, jointed together with cement, failed in the stone work. Some blocks of cement, $18'' \times 9\frac{1}{2}'' \times 9''$, were then tried in a Bramah press, and stood $58\frac{1}{2}$ tons, when the press gave way. Roman cement failed under $22\frac{1}{2}$ tons. A block of one part cement to one sand withstood 45 tons. On the 26th September some further tests were made with a better press at Messrs. Robinson & Sons, Pimlico, when the following results were obtained:—

"1. One of the previous blocks, all cement and then thirty-five days old, bore a pressure of 68 tons, when it cracked at one angle, but ultimately bore 90 tons without any alteration.

"2. An exactly similar block bore 141 tons without even a crack, and stood under that pressure for nearly one minute, when it broke.

"3. Another similar block bore 104 tons.

"4. One composed of nine sand to one cement bore $4\frac{1}{2}$ tons.

"5. One of equal quantities of sand and cement previously submitted to a pressure of 47 tons now cracked at that pressure, but ultimately bore a pressure of 108 tons before it broke down, the form of the crack not altering."

Public Attention begins to be directed to Portland Cement.—The rivalry between the two principal firms engaged in the manufacture of Portland cement, in what we may term the London district, had the effect of directing public attention to the new material, and the cement industry from this time steadily increased in importance. Fresh factories were started, and the quality gradually became more and more reliable.

Early Experiments on the Strength of Cements.—In a paper read by Mr. G. F. White before the Institution of Civil Engineers in May, 1852, there is an account of the experiments, to which reference has already been made, at Messrs. Grissell's works in 1847, and of some additional tests carried out at Mr. Jackson's works on March 8th, 1851. We quote certain of these results, as they are of importance as illustrating the relative merits of the artificial and natural cements made about that time. Each block was 9 inches square and 18 inches long, and it was tested by hydraulic pressure applied on the smaller ends, a surface of 81 square inches:—

Nature of Block.	Age in Days.	Crushing Force in Tons.		Lbs. per sq. inch.
		On 81 sq. ins.	On 144 sq. ins.	
1. Pure Portland cement,	30	75	133	2,074
2. { 1 Portland, } Immersed in water for	52	45	80	1,244
{ 2 Sand, } 7 days after making,				
3. { 1 Portland cement, } Immersed in water	52	25	44	691
{ 3 Sand, } as soon as made				
{ } for 7 days,				
4. Pure Roman cement,	30	27	48	746
5. { 1 Roman cement, }	52	3	5.33	83
{ 2 Sand, }				
6.* { 1 Portland, }	48	24	42.6	664
{ 2 Sand, }				
{ Concrete, }				
7.* Do.,	270	63.75	113.33	1,763
8.* { 1 Portland, }	70	16.875	30	442
{ 3 Sand, }				
9.* { 1 Portland, }	30	10	17.77	276
{ 10 Shingle, }				

* Experimental blocks 6, 7, 8, 9, described as concrete, of which cement and sand occupied one-fifth part in bulk.

Experiments made at Mr. Jackson's works on blocks 6 inches by 6 inches, and 12 inches long:—

Nature of Block.	Age in Days.	Crushing Force in Tons.		Lbs. per sq. inch.
		On area of 36 inches.	On the sq. foot.	
Pure Portland cement,	40	40	160	2,453
„ Atkinson's „	40	20	80	1,244
„ Sheppey „	40	19.5	78	1,213
„ Roman „	40	13.25	53	829

It is argued from the first set of experiments that neat Portland cement is three times the strength of neat Roman cement, and that with two parts of sand Portland is half as strong again as neat Roman cement, while even with three parts of sand it is equal in strength to neat Roman cement.

Experiments at the Exhibition of 1851.—Some experiments tried at the great Exhibition in Hyde Park, before the Jury of Class XXVII. in September, 1851, are interesting, as the cement was used in the briquette form (see Fig. 1).

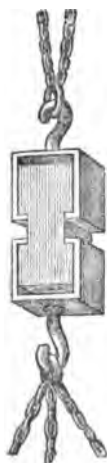


Fig. 1.

The breaking weight per square inch of neat Portland cement was 414 lbs., which is a very good result for that period. No indication is, however, given of the age of this sample.

Prices of Roman and Portland Cement.—The price of Roman cement had fallen about 1848 to 1s. 3d. per bushel, the original price having been 4s. 6d.; the cost of Portland cement at this time was, as we have seen, about 2s. 6d. per bushel.

Mr. Johnson's Statement respecting the Manufacture.—We think that we may here insert a very important statement respecting the early history of Portland cement, drawn up for one of the authors by the veteran cement manufacturer, Mr. I. C. Johnson, in 1880, extracts from which were published in *The Building News* of that year. Mr. Johnson states that young Aspdin "began work at Rotherhithe in connection with Messrs. Maude & Son on a small scale, and did sometimes make a strong cement, but owing to a want of scientific method, the quality as respects strength and durability was not to be depended upon." He proceeds:—

"I was at this time [about 1845] manager of the works of Messrs. White, at Swanscombe, making only the Roman cement, Keene's plaster,

and Frost's cement, the latter composed of 2 chalk to 1 of Medway clay, calcined lightly, and weighing 70 to 80 lbs. per bushel.

"My employers, attracted by the flourish of trumpets that was then being made about the new cement, desired to be makers of it, and some steps were taken to join Aspdin in the enterprise, but no agreement could be come to, especially as I advised my employers to leave the matter to me, fully believing that I could work it out.

"As I before said, there were no sources of information to assist me, for although Aspdin had works, there was no possibility of finding out what he was doing, because the place was closely built in, with walls some 20 feet high, and with no way into the works, excepting through the office.

"I am free to confess that if I could have got a clue in that direction I should have taken advantage of such an opportunity, but as I have since learned, and that from one of his later partners, that the process was so mystified that anyone might get on the wrong scent—for even the workmen knew nothing, considering that the virtue consisted in something Aspdin did with his own hands."

Aspdin's Secret Processes.—"Thus he had a kind of tray with several compartments, and in these he had powdered sulphate of copper, powdered limestone, and some other matters. When a layer of washed and dried slurry and the coke had been put into the kiln, he would go in and scatter some handfuls of these powders from time to time as the loading proceeded, so the whole thing was surrounded by mystery."

Analysis of Aspdin's Cement.—"What then did I do? I obtained some of the cement that was in common use, and, although I had paid some attention to chemistry, I would not trust myself to analyse it, but I took it to the most celebrated analyst of that day in London, and spent some two days with him. What do you think was the principal element, according to him? Sixty per cent. of phosphate of lime! All right, thought I, I have it now. I laid all the neighbouring butchers under contribution for bones, calcined them in the open air, creating a terrible nuisance by the smell, and made no end of mixtures with clay and other matters contained in the analysis, in different proportions and burnt to different degrees, and all without any good result."

Attempt to produce a Cement from the Components of Roman Cement.—"The question was, what was the next thing to be done? I had an idea that the elements were those contained in Roman cement, and I had read somewhere that the older chemists had taught that the value of Roman cements was due to the iron and manganese contained in them. I knew that these matters gave rise to the peculiar colour of Roman cement, but they were absent in Portland."

Mr. Johnson's Experiments.—"I had a laboratory and appliances

on the premises, so I worked night and day to find out the component parts of the stones from Harwich and Sheppey. Having found these, and having tried many experiments, spreading over some months, in putting different matters together, I began to think that lime and alumina were the chief ingredients necessary. I therefore tried quick-lime powdered and mixed with clay and calcined, by which means I got something nearer. It was a cement very much like Frost's. After this I used chalk and clay as used in Frost's cement, but with more chalk in proportion. The resulting compound being highly burned, swelled, and cracked.

"By mere accident, however, some of the burned stuff was clinkered, and, as I thought, useless, for I had heard Colonel Pasley say that he considered an artificial cement should feel quite warm after gauging, on putting your hand on it, and that in his experiments at Chatham he threw away all clinkers formed in the burning."

Trial of Clinker formerly rejected.—"However, I pulverised some of the clinker and gauged it. It did not seem as though it would harden at all, and no warmth was produced. I then made mixtures of the powdered clinker, and powdered lightly-burned stuff,* this did set, and soon became hard. On examining some days later the clinker only, I found it much harder than the mixture; moreover, the colour was of a nice grey."

Works conducted on a Larger Scale.—"Supposing that I had nearly got hold of the right clue, I proceeded to operate on a larger scale, making my mixture of 5 of white chalk to 1 of Medway clay. This was well burned in considerable quantities, and was ground finely; but it was of course a failure from excess of lime, although I did not then know the reason of it. The whole of this material was tossed away as useless into a kind of tunnel near at hand, and laid there for some months, after which I had the curiosity to take a sample of it and gauged it as before, when, to my astonishment, it gauged smoothly and pleasantly, and did not crack and blow as before, but became solid, and increased in hardness with time."

Traces a Previous Failure to Excess of Lime.—"Cogitating as to the cause of this difference, it occurred to me that there had been an excess of lime, and that this exposure in a rather damp place had caused the lime to slake.

"This was another step in advance, giving me as it did the idea of there being too much chalk, so I went on making different mixtures until I came to 5 of chalk and 2 of Medway clay, and this gave a result so satisfactory that hundreds of tons of cement so mixed were soon

* Aspdin, we learn from one of his letters, made his cement from a mixture of tender and hard-burned clinker.

afterwards made. Some of this cement was sent to the French Government Works at Cherbourg, and was, as I believe, set up as a standard of quality to which all subsequent purveyors had to conform."

Anticipates Process of Grinding with a Minimum of Water.—

Mr. Johnson subsequently explains how he partly anticipated Goreham's patent of grinding with a minimum of water, and he details his experiences as a cement maker on his own account, first at Frindsbury near Rochester (where he established the first manufactory on the Medway), then at Cliffe, later at Gateshead-on-Tyne, where he followed Aspdin, who had failed in business, and lastly at Greenhithe.

Last Traces of the Aspdins.—We think that Mr. Johnson's account is very interesting as the personal narrative of one of the founders of the cement industry, and one to whom, as we shall see later, it owes some important improvements. In bringing this somewhat lengthy chapter to a close, we may mention that the elder Aspdin was still working at Wakefield in 1853, and we are informed by his grandson, Mr. W. A. Aspdin, that he resided there until his death in 1855. He was interred at St. John's Church, Wakefield, and his tombstone there bears the following inscription:—

"Sacred to the memory of the late
JOSEPH ASPDIN,
of this town,
Inventor of the Patent Portland Cement,
Who departed this life on the 20th day of March, 1855,
Aged 76 years."

His grandson tells us, moreover, that the works he originally built were pulled down for the railway, and other mills were erected, which were carried on after his death by his son James. Joseph Aspdin had two sons and one daughter. His son William, after his failure at Gateshead,* went to Germany, and died in Holstein, during the Schleswig-Holstein war in 1864.

* A writer in *The Builder*, in March, 1880, states that, before the success of Aspdin's new material was thoroughly assured, "he launched out by renting several acres of land near Gravesend, and commenced building 'Portland Hall' in such an elaborate and artistic manner as to require some £40,000 to bring it to completion. When the structure was rather more than one-third up, he had to stop, and he sold off at so great a sacrifice that he left the country and died abroad."

CHAPTER V.

THE COMPOSITION OF PORTLAND CEMENT.

CONTENTS.—Influence of Materials on the Seat of the Trade—Essential Components of Cements—Proportions of Ingredients—Over-limed Cements—Danger of Highly-limed Cements—Less Important Constituents of Cements—Sulphur in Cement—Iron in Cement—Magnesia and its effects on Roman and Rosendale Cements—Alkalies.

Influence of Materials on the Seat of the Trade.—The inducements originally offered to cement makers to settle in the Thames district are easy to understand, the ample supply of chalk, and the excellent Medway mud, were admirably adapted for their purpose, and, in course of time, a large colony of manufacturers established themselves on the estuary of the Thames, and the London Portland cement obtained a wide reputation. Indeed, the belief gained ground that no really good cement could be made elsewhere, and the raw materials of this district were transported at great expense to other less-favoured localities, in which the manufacture was carried on.

Failures caused by want of Chemical Knowledge.—Owing to the imperfect knowledge of the chemistry of cements, the process was at first, as we have seen, exposed to continual dangers, and the failures of the cement made from the lias and from the lower chalk were at one time so serious as to appear likely to bring all other cements into discredit. The constant fluctuations in the composition of the thin beds of stone and shale in the lias formation, and the varying quantities of clay combined with the lower or grey chalk led the cement maker who relied upon rule-of-thumb into all kinds of difficulties and dangers. Too often he depended upon some cunning workman, who made a mystery of his proportions, and concealed his ignorance and accounted for his failures by statements which the master took upon trust or did not venture to dispute.

An Early Authority on Cement Making.—We remember, in the early sixties, such an authority in one of the older works on the Medway, who had washed whole backs full of over-limed slip (the liquid mixture of chalk and clay), and who attributed the “blowing” of the resultant cement to an unpropitious state of the atmosphere. The real fact of the matter being that some new beds of chalk were being quarried which contained only 5 per cent. of clayey matters, instead of the 10 per cent.

present in the chalk to which he was accustomed, and he had dealt with the new chalk just as he did with the old.

Materials available for Cement Making.—It is now perfectly well known that suitable mixtures of carbonate of lime and clay can be prepared from raw materials, to be found in all parts of the world, and in many geological formations. It is not essential that the mixture should be made of each of these substances in the pure state. They occur naturally compounded in various proportions in vast beds in many different localities, and in making use of such materials, all that is necessary is to employ them in such proportions as will give the required quantity of carbonate of lime in the mixture.

As examples of pure or nearly pure materials, we may instance the white chalk of the Thames district, the indurated chalk of the north of Ireland, and many deposits of the carboniferous limestone formation, all of which contain about 98 per cent. of carbonate of lime. Among the clays and shales in use for cement making (under the latter term we imply a solid form of clay compacted by pressure and capable of being split into laminæ), we have the alluvial mud of the Medway—a salt-water deposit—the fresh-water alluvium found on the banks of many rivers, boulder clay, the shales and clays of the coal measures, and the shales of the Silurian formation, in which last lime is either entirely absent or present in very small quantities. As instances of naturally compounded materials, we may mention the lower or grey chalk of the Medway, the limestones and shales of the lias and of the upper carboniferous strata, gault clay, the chalk marls of Cambridgeshire and Germany, and the Silurian limestones now so widely used in the Lehigh Valley district of Pennsylvania.

The Present Position of the Cement Manufacture.—From the point of view simply of materials, we have now entered upon a phase of the Portland cement manufacture in which the trade has passed far beyond the boundaries of the Thames and Medway districts, and when even the lias formation has ceased to present its former attractions to the cement maker. Since, as we have seen, it has become a matter of common knowledge, that chalk is not an essential factor in the production of a good sample of Portland; moreover, with the growth of skill and chemical knowledge, manufacturers fight shy of the treacherous and uncertain beds of the lias formation, many of the shales in which contain so much iron pyrites and sulphur in other forms as to render them wholly unsuitable for the production of a really first-class sample of Portland. The factories established at various seaports in the north, where chalk could readily be obtained at low freights as a return cargo, are working at a great disadvantage as regards cost of raw materials, and in some cases have been closed. The tendency nowadays is rather to seek for a cheap and

abundant source of raw materials, and to establish works in the immediate vicinity of large centres of population, where the cement is likely to be locally required.

The Constituents of Cements.—It may be as well, before we attempt to treat of the various processes of manufacture, if we examine somewhat in detail the actual constituents of cement, calling attention, first, to those substances the presence of which in Portland is essential, and subsequently to certain other ingredients which either exert no influence upon the mixture, or which in certain cases, or when they exist in large quantities, may be productive of positive injury to the cement.

Essential Components of Cements.—Careful experiments have proved that the only essential components of a cement are lime, alumina, and silica, which substances we have dealt with in our introductory chapter; but there are, secondly, as we have seen, numerous other ingredients present in Portland, occurring either as impurities in the clay, or in certain cases derived from the fuel used for calcination, some of them tending to facilitate the cement action, others either inert in themselves or merely taking the place of the essential constituents, and lastly certain substances which we must regard as injurious, except when they are found in very small quantities.

Characteristics of Clays adapted for Cement Making.—The best clays for the use of the cement maker are those which are highly siliceous, even if much of the silica occurs in the free state as fine sand. Should the silica be present as a coarse-grained sand, the mixture requires to be very perfect and finely ground. Experience shows that in the finished cement the silica, even from a sandy clay, is found in the soluble form. This is not the case in burning such clayey substances into a hydraulic lime, as the temperature reached is not sufficiently high to effect this change. The proportion of silica present should at least equal $2\frac{1}{2}$ times the amount of the iron oxide and alumina taken together. Thus a clay containing 18 per cent. of alumina and 6 per cent. of ferric oxide should contain at least 60 per cent. of silica. Clays of this composition require a high temperature to effect their fusion when they are employed in conjunction with carbonate of lime. The resulting cement sets in a reasonable time, speedily attains sufficient strength to show good breaking tests, and steadily increases in strength with age. On the other hand, clays with a high percentage of alumina yield a much more fusible mixture, which can be calcined with less fuel, but which often causes trouble in the kiln by overburning. The finished cement sets quickly, often indeed with such rapidity as to render its use difficult without regauging, and the strength at short dates runs high. There is little increase with age, indeed often a tendency to retrograde action.

Proportions of the Ingredients.—The exact percentage of clay which, when of the right quality, may be added to the carbonate of lime to produce Portland cement varies between somewhat wide and not very clearly defined limits. All mixtures which contain, say, from 74 to 77 per cent. of carbonate of lime will, when very carefully and intimately mixed and very finely ground, produce, if sufficiently calcined, a Portland cement of fair quality. When the percentage of clay runs too high—that is, when the carbonate of lime in the dried “slurry,” or mixture of lime and clay, falls below 74 per cent.—a cement is obtained which is technically termed “over-clayed.” Compounds of this nature fuse or “run” in the kiln at a temperature below that required for the production of a sound “clinker” (the term applied to the fused material issuing from the kiln). The resulting cement is light in weight, is apt to set quickly, has a brownish colour, and never becomes thoroughly indurated. These light descriptions of Portland, moreover, have a tendency to crumble on exposure to the weather.

Light Cements well adapted for Plasterer’s Work.—They are essentially plasterer’s cements, as they work readily under the float or trowel, and, owing to the fact that they set more speedily than a dense cement, the workman can leave them within reasonable time, which he appears very often to be unable to do when using a dense slow-setting sample of Portland. These over-clayed cements are now but rarely made, though at one time they were much sought after and preferred for certain descriptions of work. There is, however, now but little demand for cements of this type, which in some cases approached the Roman cements in composition, since the finely-ground Portland now made sets sufficiently quickly for all practical purposes. It was the fraudulent substitution of cements of defective quality of the above character, prepared from slack-burnt clinker, for dense Portland which, for a time, had a prominent share in bringing this excellent material into disrepute. There was formerly, when the characteristics of Portland were less widely known, a great temptation to aim at the production of these light cements, as they are ground with comparative ease, and they enable the cement maker to dispose of his insufficiently burned material without further calcination.

Over-limed Cements.—The presence of an excess of lime, on the other hand—that is, where the proportion of carbonate of lime in the slurry ranges above 77 or 78 per cent.—leads to the production of a cement which will stand the highest temperatures in the kiln, and in fact necessitates very heavy firing. Such cements, technically termed “over-limed,” are extremely dense when burnt at a high temperature, they set very slowly, and are very difficult to grind. The sample of Portland produced from a mixture of this kind is apt to be treacherous when used in construction—i.e., unless it has been properly “purged” or exposed in

thin layers to the atmosphere to cause the limey particles to become air slaked, and it is liable to "blow" or swell in the work; an action very frequently caused by the retarded hydration of certain of its particles.

Danger of Highly-limed Cements.—Looking to the great tensile strength and the density now demanded under certain specifications, manufacturers are induced to raise to the utmost limit of safety the percentage of lime, and thus to approach more and more to the danger point above indicated, a danger only avoided by extremely fine grinding and careful purging. Manufacturers of cement are well aware of the risks encountered in producing cements with high percentages of lime, and it is usual to store Portland cement for some considerable time in the warehouse before it is sent out for sale. Many specifications involve a further storage on the works of the contractor previous to use, and even the best samples of Portland improve under this treatment. Apart from considerations of safety, there is a real gain to cement producers in the storage of Portland cement, either as clinker or in the ground state, for some considerable period previous to sale.

Less Important Constituents of Portland Cement.—The colour of Portland cement is due to the iron oxide, which is always present, and belongs to the second of the categories under which we have grouped the components of cements, which comprises also magnesia and the alkalies. In the last class we must include the sulphur compounds, as also the carbonic acid and water; these two last-named ingredients, if found in any quantity, indicate either that the sample of cement is very stale or that the mixture has been imperfectly calcined. We propose now to discuss briefly the action of sulphur, sulphuric acid, magnesia, iron oxides, and the alkalies.

Sulphur in Portland Cement.—The sulphur of Portland cement is derived mainly from two sources, either from the clay or clay-shales, which are often more or less impregnated with calcium sulphate, and which contain, especially in the case of the lias clays, nodules of pyrites or sulphide of iron, or from the coke employed for the calcination, which, when it is obtained from the gas works, is always rich in sulphur compounds. Gas coke, on account of its relative cheapness, is commonly used by cement makers, and English cements almost invariably contain a certain amount of sulphur derived from this source.

Percentage of Sulphur allowable.—Sulphur, when it exceeds certain not very sharply defined limits, is undoubtedly injurious to Portland cement. Its action upon cements is a matter of very considerable importance, and has scarcely received the attention which it deserves. Some authorities recognising its detrimental effects upon cement have attempted by carefully worded specifications either to exclude it altogether, or to limit the quantity present to 1 or at most

2 per cent. of calcium sulphate, a degree of purity seldom if ever attained in the case of English-made cements. In the German standard rules (see Appendix E) the beneficial effect of small quantities of calcium sulphate upon Portland is so far recognised that manufacturers are allowed to employ a proportion not exceeding 2 per cent. in order to confer slow-setting properties.

Selenitic Action.—This action of the calcium sulphate was discovered by the late Major General Scott, C.B., the inventor of selenitic cement in 1854, and in the so-called Scott's cement, patented by him in 1856, this property was, for the first time, turned to commercial account. To General Scott, moreover, we owe the proposal to add calcium sulphate to Portland cement for the purpose of retarding the setting. We shall treat of the selenitic cement in a special chapter.

Sulphuric acid, when present in Portland cement, acts, it is believed, in the manner described in the case of Selenitic cement upon the uncombined lime present and deprives it of its avidity for water, causing it to set after the nature of a cement. Very small quantities of sulphuric acid will delay the rapidity of the initial set of Portland cement, and we have found, in the case of a fiery cement, that the addition to it of 1 per cent. of its weight of plaster of Paris would delay the time needed to set from five to seven hours.

Messrs. Dyckerhoff's Experiments.—The annexed table, extracted from the *Proceedings of the Inst. of Civil Engineers*, gives the results of some important experiments by Messrs. Dyckerhoff bearing upon this question. They demonstrate that, together with the delayed setting time, a great gain in strength results from the use of trifling additions of gypsum. In fact, this treatment is equivalent to, and may replace the purging which dense highly calcined cements require previous to use; this statement being clearly proved by the bottom row of figures. General Scott pointed out that the same results might be obtained by exposing the cement for a few minutes to the action of a jet of steam which rapidly hydrates the free lime. Indeed, in one of his numerous patents he specifies this process.

Excess of Calcium Sulphate is Injurious.—Although the action of calcium sulphate in small quantities is thus shown to be beneficial, there can be no doubt but that the presence of this substance in proportions exceeding, say, 4 to 5 per cent. of the volume are injurious, for we must remember that calcium sulphate is comparatively soluble in water, and in damp situations much of it would inevitably be washed out of the mortar, and, moreover, this substance never attains to any considerable degree of hardness.

TABLE SHOWING GAIN IN STRENGTH WHICH RESULTS FROM AN INCREASE IN SETTING TIME.

No.	SAME KIND OF CEMENT.	Time of Setting Neat. Minutes.	Neat Cement 25 parts Water to 100 parts Cement.					One Cement to three of Standard Sand.				
			One Week.	Four Weeks.	Twelve Weeks.	Twenty-five Weeks.	Fifty-two Weeks.	One Week.	Four Weeks.	Twelve Weeks.	Twenty-six Weeks.	Fifty-two Weeks.
1.	Original Cement, . . .	20	322.9	405.5	517.9	621.7	701.4	115.2	167.9	237.6	301.6	359.9
2.	The same Cement with $\frac{1}{4}$ per cent. of Gypsum, . . .	210	315.8	456.7	573.4	624.6	651.6	142.3	212.0	338.6	352.8	389.8
3.	The same Cement with 1 per cent. of Gypsum, . . .	600	375.6	507.9	567.7	697.2	781.1	159.3	237.6	311.6	368.5	384.2
4.	The same Cement with 2 per cent. of Gypsum, . . .	840	425.4	543.5	688.6	718.5	806.7	180.7	263.2	304.4	374.2	409.7
5.	The same Cement without Gypsum but kept in store for some months, . . .	630	317.3	449.6	550.6	593.3	618.9	167.9	219.1	318.7	359.9	431.1

Note.—No. 1 weighed about 110.7 lbs. per bushel. No. 5 about 105.9 lbs. per bushel of 40 litres.

The breaking weights are given in lbs. per square inch.

Deleterious Action of Calcium Sulphide.—There is a great objection to the presence of sulphates and sulphur compounds in the raw materials for cement, and this is owing to their tendency to become decomposed in the kiln, leading to the formation of calcium sulphide, a most dangerous ingredient of Portland cement. The troubles that arise from the calcium sulphide are probably mainly due to its liability to attack and decompose the iron compounds in the cement.

Slag Cement.—In the case of cements made from mixtures of lime and blast-furnace slag, there is always a notable proportion of calcium sulphide present, and the action of this sulphide upon the iron gives to most of these cements the unpleasant green colour to which reference is made in the next paragraph.

Iron in Portland Cement.—Iron is found in well-burned Portland cement chiefly in the condition of the lower oxides, but there is nearly always a certain proportion of the peroxide present; and French chemists speak with certainty of combinations with lime in which the iron acts as an acid to form the so-called ferrites of lime. With certain of the iron compounds the sulphur from the calcium sulphide reacts, leading to the formation of iron sulphide. This substance slowly attracts oxygen, and becomes converted into sulphate of the protoxide of iron, which subsequently further oxidises and assumes a brownish-red colour. This action goes on with much greater rapidity in the gauged cement than it does before the cement is made up. Test samples when broken have a greenish tint, much more highly coloured than we should expect in a good specimen of Portland, and the fractured surface on further exposure to the atmosphere turns to a rusty brown. If the test briquettes are immersed in water they never harden as they should do, especially if made up with sand, and though at first their colour is greenish, it changes to brown as before, on being taken out of the water and exposed to the air. The set of cements of this type is very slow, even when water is very sparingly used in gauging them, and with an excess of water they will scarcely set at all. There can be but little doubt that the presence of iron in this form hinders the crystallisation of the mass, and cement of this character never attains a high degree of tensile strength, especially under the sand test.

Magnesia in Cement.—Nearly all specimens of Portland cement contain a small amount of magnesia, this substance being generally present in the chalk, in the mud from the estuaries of the Thames and Medway, as also in the clay shales of the lias formation.

The magnesia is originally found in combination partly with carbonic and partly with silicic acid, but some clays contain small quantities of magnesium sulphate. In the process of calcination the carbonic acid is expelled, leaving caustic magnesia, a substance which behaves in the cement in a similar way to the uncombined lime. It has, how-

ever, much less avidity for water than the lime has, and becomes hydrated much more slowly.

Experiments of Mr. Jones on Action of Magnesia.—From some experiments quoted in a paper read by Mr. W. Smith before the Institution of Civil Engineers, to which we shall refer later, and which were carried out by Mr. H. T. Jones, of Aberdeen University, 100 parts of magnesium oxide combined with water at the following rate :—

In twenty-four hours,	36.00 per cent.
„ forty-eight hours,	38.74 „
„ nine days,	44.30 „

The theoretical maximum needed to completely hydrate the above quantity of magnesium oxide was 45.00 per cent. It is not stated at what temperature this oxide was produced, but the hydration was in this case fairly rapid, and the calcination was doubtless effected with far less heat than that needed to burn Portland clinker. Mr. Smith tells us that on adding 5 per cent. by weight of this dehydrated magnesium oxide to Portland cement there was a loss in strength, when tested after nine days, of 20 per cent. Made up with 3 parts of sand, the cement and magnesia broke at 162 lbs. per square inch in twenty-eight days, but no corresponding test is given with unmixed cement. The fact of adding this quantity of magnesia to the sample of cement after calcination does not, we think, throw any light upon the subject.

Time Needed for Hydration.—The time occupied by magnesia in solidifying the water is, as is well known, proportionate to the temperature to which it has been exposed in the kilns. It will readily be seen that this fact indicates a source of possible danger in cements calcined at a very high temperature, for we can conceive of cases in which the hydration of the lime and the combination with silica and alumina to form hydrated silicates may have been completed before the magnesia has taken up its water of hydration. As this action is accompanied by increase of volume, the tardy slaking of the particles of magnesia may lead to the disruption of the cement mortar. This action does actually take place, and in the case of certain cements of French origin, in which a dolomitic lime was used containing as much as 25 per cent. of carbonate of magnesia, the expansion of the mass continued for several months after the mortar was made up and brought the material into so much disrepute that the manufacture had to be abandoned.

Compounds of Magnesia with Silica and Alumina.—The compounds formed by magnesia with silica and alumina resemble in every respect the similar silicates and aluminates of lime, and the affinity between the silicic acid and the magnesia is greater than in the case of lime; but, as M. Fremy has pointed out, there is strong reason to believe that these substances also become hydrated much more slowly than the lime compounds, and from this circumstance it follows that mortars which

consist of a mixture of the silicates and aluminates of lime and magnesia may, after the initial set of the lime, undergo molecular changes, due to the retarded hydration of the magnesia compounds, which may further disturb the original cohesion of the mass and lead to disruption.

Magnesia Compounds are Hydraulic.—It has, however, been found by laboratory experiments that the silicates and aluminates of magnesia acquire on hydration a superior degree of hardness to the similar compounds of lime, and that they remain wholly unaltered under water.

Influence of Magnesia on Cements.—When the percentage of magnesia in the cement is small—say under 3 per cent.—and when the purging or air slaking has been allowed to take place, no injury need be apprehended, but in all dense highly-burned cements, the action of the magnesia must be carefully watched. We do not anticipate any difficulties if the magnesia is combined with sulphuric acid as this compound does not become altered in the kiln.

Roman and Rosendale Cements.—In the tender-burned cements of the Roman cement type and in the Rosendale cement of the United States of America, described at p. 25, the magnesia is found to be quite harmless. It should be remembered while treating of the magnesia that this substance by itself is perfectly hydraulic, and calcined magnesia will set in water and produce a stone-like mass. But for this purpose it should be calcined at a cherry red heat or at a very moderate temperature, and it must be ground to a fine powder before use.

Large amount of Magnesia present in American Cements.—It will be seen from the annexed analyses of American cements of the Rosendale type that many of these materials contain a large percentage of magnesia in addition to lime and alkalis, and that the proportion of silica and alumina is low as compared with our English quick-setting cements, as, for instance, those made from the septaria of Harwich and the Isle of Sheppey, some analyses of which are added for the purpose of comparison.

ANALYSIS OF NATURAL CEMENTS.

	Layer No. 2. Rosendale.	Layer No. 13. Rosendale.	Layer No. 17. Rosendale.	Sheppey Island. Septaria.	Harwich. Septaria.
Carbonate of lime, . . .	43·30	28·48	40·00	63·00	60·5
Carbonate of magnesia, . .	26·04	32·86	39·04	4·2	5·7
Silica, clay, and insoluble silicates,	18·52	26·00	11·10	} 32·00	} 33·0
Alumina,	2·18	4·64	2·52		
Peroxide of iron,	1·86	1·86	1·42		
Sulphuric acid,	1·96	1·18	0·22		
Potash and soda (chloride), .	4·24	4·72	4·06	0·8	0·8
Water and loss,	0·20	0·26	0·26	...	...
Total,	98·30	100·00	98·62	100·00	100·00

Controversy Respecting the Action of Sea Water on Cement.—

The presence of magnesia as a constituent of Portland cement has attained considerable notoriety, in consequence of the partial failure of the great harbour works at Aberdeen, attributed by Mr. Messent, Prof. Brazier, and others, to the action of the magnesia in the sea water. This subject was brought under the notice of the members of the Institution of Civil Engineers in a paper by Mr. Wm. Smith, in 1891, and occasioned a most interesting discussion on cement action. We give in Appendix B a brief outline of the above paper and of the discussion that followed, which traverses the whole ground of the controversy.

Alkalies in Portland Cement.—We have still to glance at the action of the alkalies which we regard as very important constituents of the cement. The only alkalies found in Portland and nearly always present in good samples, to the extent of from 0·5 to rather over 1·0 per cent., are potash and soda. These substances are derived mainly from the clays or clay shales, and while their action is most valuable during the calcination they are also beneficial, we believe, at the time of gauging the cement, for the alkaline silicates, as it is well known, are the only compounds with silica soluble in water. Their office as carriers of silicic acid to the lime and other sparingly soluble ingredients of the cement has, we think, not hitherto been sufficiently studied, and when considering the set of cements and the recent theories respecting this much debated question, the alkalies should not be overlooked.

The Investigations of Fuchs.—It will be sufficient here to allude briefly to the investigations of Fuchs, who demonstrated very clearly the influence of these substances. Thus he found that decomposed felspar when treated in the humid way with caustic lime parted with 10 per cent.—that is to say, nearly the whole—of its potash; he found further that substances containing but little alkaline matter, such as pumice-stone and pitch-stone, were deprived of the same by lime, and that both lithia and potash could be separated in this manner from lepidolite (a silicate of alumina, lithia, and potash). By a similar process the alkali is separated from most varieties of clay and transferred to the lime. The solubility of alumina and gelatinous silica in potash renders it more than probable that the alkalies accelerate the hydraulic action of the lime by promoting and facilitating the gradual transference to it of the silica.

Kuhlmann's Experiments.—Kuhlmann carried out numerous experiments with the alkaline silicates constituting "water-glass," which established the fact that these materials part with their silica to the lime without the aid of heat, and the same reaction occurs with carbonate and sulphate of lime as with caustic lime—the alkali transfers its silica to the lime and unites with the carbonic or sulphuric acids. Chalk powder exposed to a solution of silicate of potash becomes after a short time

solidified into a stone-like mass, and a lump of chalk immersed in the liquid receives a surface coating of silicate of lime, which on subsequent exposure to the air becomes so hard that it is capable of taking a polish. The induration of cement concretes by means of the so-called "silica-bath" depends upon this property, and the preservation of wall surfaces by a coating of water-glass is another illustration of this principle.

Portland Cement Manufactured from Fused Clinker.—It has always been hitherto maintained by cement experts that, in order to produce a perfect sample of Portland cement, the raw materials must be raised to the temperature of incipient fusion, but that it was fatal to exceed this temperature and to fuse any considerable portion of the mass. Indeed, in many works, the accidentally vitrified clinker was picked out and rejected. This opinion has, however, of late been somewhat rudely assailed, and it is now asserted that by suitably selecting the constituents and by burning them at a temperature capable of melting them into a slag, such as is produced in the blast furnace, the product obtained is superior to that prepared in the ordinary way in the cement kiln. Experiments conducted in America at the Atlas Portland Cement Works with this process are still in progress, but it may be remembered that excellent results have been obtained both in Germany and in the United States in manufacturing cement from a mixture of finely-ground blast-furnace slag and limestone in the manner we have described in our chapter on *Slag Cements*. It is evident that the silicates produced at the temperature of the blast furnace can readily be decomposed in the presence of lime at the heat needed for the production of cement clinker, and there is no chemical difference between the clinker produced from a mixture of fused silicates, as contained in iron slags, and that resulting from carbonate of lime and clay as prepared in the ordinary way.

CHAPTER VI.

**THE CHEMICAL ANALYSIS OF CEMENT RAW MATERIALS,
PORTLAND CEMENT, AND LIME.**

CONTENTS.—Limestone and Portland Cement Mixtures—Determination of Silica—Iron—Alumina—Lime—Magnesia—Sulphur—Alkali Metals—Chlorides—Carbon Dioxide—The Analysis of Clay and Shale—Analysis of Portland Cement—Analysis of Lime—Atomic Weights and Factors.

Limestone and Portland Cement Mixtures.—The method to be described is applicable to any material containing not less than 70 per cent. of carbonate of lime. If the carbonate of lime falls below this amount, the analysis is best made by one of the methods described for clay. The sample should be finely powdered, dried for some hours at a temperature of 100° C., and transferred to a stoppered weighing tube, from which, when cold, the following quantities are weighed off:—

1. From 0.5 to 1 gramme for the determination of sand, silica, iron, alumina, lime, magnesia. This quantity to be transferred to a platinum crucible.

2. About 2 grammes for total sulphur, transferred either to a flask or a platinum crucible, according to which method of determination is decided upon.

3. From 1 to 2 grammes for sulphuric acid, transferred to a beaker.

4. About 4 grammes for potash and soda, to be transferred to a platinum crucible of ample capacity.

5. About 1 gramme for carbon dioxide, transferred to the evolution flask of the apparatus employed for the determination.

Quantity No. 1—Determination of Total Silica.—Gently rap the crucible once or twice on the bench to consolidate its contents, which should not be again disturbed, and ignite it, first at a gentle heat, and then strongly for from forty to fifty minutes in the full heat either of a muffle furnace or of a blast-lamp. With a foot-blower this last is rather a tedious operation, and we prefer to use a Swedish blast-lamp with a vertical flame which burns ordinary paraffin. If compressed air is available in the laboratory, the ordinary blast Bunsen burner may of course be employed, and this is quite as convenient as the Swedish lamp. By this treatment the silicates are decomposed by the action of the lime, while the sand is practically unacted upon. When cold, the contents of the crucible are turned out into a platinum dish and triturated with a little water until all tendency to set has disappeared, using either a stout glass rod with

rounded end, or, better, a small agate pestle. Add dilute hydrochloric acid in slight excess, and digest for a few minutes at a gentle heat. The crucible is rinsed with a little dilute hydrochloric acid, and washed out into a dish. If the contents have not been disturbed, they will be found after ignition to have become slightly consolidated, and will drop out of the crucible in a lump, leaving only a small quantity behind. Evaporate the contents of the dish to dryness (a water bath is safest), and complete the drying by heating the dish in a hot-air oven for two hours at 150° C. When cold, moisten the contents of dish with strong hydrochloric acid, cover with a clock glass, and set aside for fifteen minutes. Add water, stir and break up any lumps if present, heat, filter, and wash precipitate well with hot water.

One evaporation is not sufficient to entirely separate the silica. The filtrate is evaporated to dryness, and treated exactly as in the first instance, the silica being collected and washed on a separate filter. Both precipitates are strongly ignited over the blast-lamp in a platinum crucible and weighed.

Separation of Sand from the Silica previously in Combination with Bases.—The contents of the crucible are carefully transferred to a platinum dish and heated to boiling for some time, with a strong solution of sodium carbonate. The contents of the dish are allowed to settle for a minute or two, after which the clear liquid is decanted through a small filter. The residue is again treated in the same manner with sodium carbonate solution, and the operation is repeated until it does not seem to decrease in bulk. The filter is kept well washed with hot water, and it is by preference enclosed in a hot-water jacket. The contents of dish are finally removed to the filter, and repeatedly washed with hot water. If the washing proceeds slowly, it is probable that the solution, while filtering, has deposited silica in the gelatinous state upon the filter. In this case the precipitate should be washed out of the filter into the platinum dish, and again boiled with solution of sodium carbonate. It is always safest to pursue this course, as the silica has a great tendency to separate as the solution cools. The precipitate is again filtered off and repeatedly washed with hot water, then with water slightly acidulated with hydrochloric acid, finally with pure hot water. It is then strongly ignited over the blast-lamp in a platinum crucible and weighed. Its weight, deducted from that previously found, gives the weight of the silica previously combined with bases, together with any free soluble silica that may have been present in the original substance. The examination of this precipitate will be referred to further on.

Determination of Iron and Alumina.—To the filtrate from the silica add a little bromine, and boil. Allow the liquid to cool, add ammonium hydrate in very slight excess, and again boil the liquid. The precipitate

of ferric and aluminium oxides settles badly, but filters rapidly, even without the aid of a suction apparatus, and nothing is gained by allowing it to settle and washing by decantation. Wash it once or twice on the filter with hot water, setting aside the filtrate and washings, which should be collected in a beaker of ample capacity. The precipitate is washed out of the filter into the beaker in which the precipitation was originally effected, and should be dissolved in a little dilute hydrochloric acid, with the addition of bromine. Ammonium hydrate is added in very slight excess, and the solution with precipitate is boiled. The precipitate is filtered off and well washed with hot water, the filtrate and washings being received in the beaker containing the filtrate from the first precipitation. Care should be taken that this precipitate is sufficiently washed, as it retains traces of lime with great obstinacy. A small quantity of the washings should be collected in a test tube, to which a drop of ammonium oxalate is added, the contents of the tube are boiled, and the tube with contents cooled by immersion in water, as traces of calcium oxalate do not separate from a hot solution. If lime is present, the contents of the test tube are rinsed into the beaker containing the filtrate, and the washing is continued until a sample of the washings gives no trace of lime when tested as described. The second precipitation should never be omitted. The precipitate of ferric oxide and alumina is dried, strongly ignited in a platinum crucible, allowed to cool, and weighed. The filtrate is heated to boiling, sufficient boiling solution of ammonium oxalate being added to convert all the lime and magnesia present into oxalates, and the boiling is continued for two or three minutes. This produces a granular precipitate which settles rapidly. The beaker with contents is set aside for a few hours.

Separation of Iron and Alumina.—The ignited precipitate of mixed oxides is fused in a platinum crucible with acid sulphate of potassium at a low temperature. The melt is dissolved in hot water with a little dilute sulphuric acid, and is transferred to a flask fitted with an evolution tube in which is a Bunsen valve. The solution is reduced by zinc, and the iron is determined by titration with permanganate. The alumina is taken by difference. The results obtained by this method are not absolutely accurate, but are sufficiently so for technical purposes. Disturbing causes are the presence of small quantities of titanium, phosphorus, and also manganese, if the precipitation has been effected in the presence of bromine. It is best to use bromine and separate it here, as it would otherwise appear in the precipitates of lime and magnesia. If necessary, as perhaps in the case of Roman cement, it may be determined in a separate portion by the basic acetate method. Titanium is reduced by the action of nascent hydrogen; hence, if zinc is employed to reduce the solution, the result for iron will be slightly high. Exact

results may be obtained by reducing with hydrogen sulphide, boiling off the excess in a stream of carbon dioxide and titrating with permanganate. The titanium may be determined in the solution after titration for iron, by Weller's colorimetric method.*

If preferred, the iron may be determined gravimetrically by the following method:—The solution containing the mixed oxides, after fusion, is allowed to fall drop by drop with constant stirring into a strong hot solution of pure sodium hydrate, contained in a porcelain, or, better, a platinum dish. The contents of the dish are boiled, diluted considerably with water to avoid destruction of the filter paper, filtered, and the precipitate is repeatedly washed with hot water. It is very difficult to free it from adhering alkali. After well washing it is washed out of the filter, dissolved in a little dilute hydrochloric acid, ammonium hydrate added in very slight excess, boiled, the precipitate filtered off, well washed, dried, ignited, and weighed. There is always a risk that this precipitate may contain traces of alumina, and for very accurate work we prefer to precipitate the iron a second time with sodium hydrate, well washing the precipitate, and finally precipitating with ammonium hydrate.

If it is desired to estimate the alumina directly, the precipitate of mixed oxides filtered from the solution containing the lime and magnesia is not ignited, but is dissolved in a little dilute hydrochloric acid, and the iron is determined as above. The filtrates and washings are rendered acid with hydrochloric acid, a crystal of potassium chlorate is added to destroy any organic matter which might be present, and which would interfere with the complete precipitation of the alumina, and the solution is concentrated considerably. Ammonium hydrate is added drop by drop until the solution is just alkaline, and it is then boiled until a strip of moist turmeric paper held in the steam does not become brown. The precipitate is filtered off, repeatedly washed with hot water, dried, and ignited strongly over the blast lamp in a platinum crucible until the weight is constant.

Determination of Lime.—The supernatant liquid from the precipitate of calcium oxalate is decanted over a filter, and the precipitate is washed two or three times by decantation. It is dissolved by heating with dilute hydrochloric acid, the solution is rendered alkaline with ammonium hydrate, and boiled after addition of a few drops of ammonium oxalate. The beaker with contents is set aside for a couple of hours, the clear liquid decanted over the previous filter, the precipitate washed two or three times by decantation, finally transferred to filter, and well washed. The precipitate should be washed with cold water, as it is slightly soluble

* *Ber. Deutsch. Chem. Gesell.*, 1882, vol. xv., p. 2593, abstracted in the *Journal Society of Chemical Industry*, 1882, vol. i., p. 506.

in hot water. It is dried, strongly ignited over blast-lamp in a platinum crucible to constant weight, and weighed as caustic lime.

If preferred, the lime may be weighed as carbonate. The precipitate is dried in the steam oven, separated as far as possible from the paper which is completely incinerated in a coil of platinum wire, and together with the ash of filter gently heated to very low redness in a platinum crucible. Care should be taken not to overheat the crucible. The transition from oxalate to carbonate is indicated by the blackening of the precipitate, the colour of which immediately afterwards changes to white. The contents of crucible are, when cold, moistened with a saturated solution of ammonium carbonate, and carefully evaporated to dryness at a gentle heat. The crucible is then heated short of redness, and when cold is weighed with its contents.

Determination of Magnesia.—The filtrate and washings from the calcium oxalate are concentrated until ammonium salts—formed during the progress of the analysis—begin to crystallise out. To save time this operation may be commenced as soon as a sufficient quantity of filtrate has been obtained from the first precipitation of the lime. The ammonium salts are best expelled before precipitating the magnesia. To effect this two methods are available.

1. The concentrated solution is washed into a flask, strong, pure, nitric acid is added, and the flask is gently heated. A violent reaction takes place on heating, and the decomposition of the ammonium salts is complete when the reaction ceases, and is not repeated on the addition of a few c.c.s. of nitric acid. The contents of flask are boiled down, carefully evaporated to dryness on a sand-bath, heated with a little water and a few drops of hydrochloric acid, and washed out into a small beaker.

2. The concentrated solution is transferred in small quantities to a platinum dish, carefully evaporated to dryness, and gently ignited until the ammonium salts are entirely expelled. The residue is heated with water and a few drops of hydrochloric acid.

The hydrochloric acid solution in either case is rendered distinctly alkaline with ammonium hydrate. Should a milky precipitate separate, it consists of magnesium hydrate, and a few drops of ammonium chloride solution should be added to dissolve it. Two drops of ammonium oxalate solution are added to ensure the complete separation of lime, and the solution is boiled. A slight white precipitate separates in flocks. It consists mainly of silica and alumina, principally derived from the glass and porcelain vessels used for the analyses. Manganese, if present, will be separated here. Its presence is indicated by the precipitate turning brown on exposure to air. When cold the solution is filtered and the precipitate is disregarded. The magnesia is now present in a clear concentrated solution, free from excess of ammonium salts. It is rendered

strongly alkaline with ammonium hydrate, solution of sodium phosphate is added in excess, the mixture is well stirred and set aside for twelve hours. The precipitate is filtered off and washed with a mixture of 3 parts water and 1 part of strong ammonium hydrate until a few drops of the filtrate, rendered slightly acid with nitric acid, give no opalescence on the addition of a few drops of a solution of silver nitrate. The precipitate is dried, separated from the filter, and transferred to a platinum crucible. The filter is completely incinerated in a coil of platinum wire, the ash being allowed to fall upon the precipitate. The crucible is ignited, at first gently, finally at the full heat of the blast-lamp. The magnesia is weighed as pyrophosphate.

Some analysts do not remove ammonium salts, but precipitate magnesia in the mixed filtrates and washings from the lime after concentration to a moderate bulk. When time permits and for accurate work they should always be got rid of by one of the methods described as a cleaner precipitate is thereby obtained. Now that many specifications limit the quantity of magnesia in Portland cement, often allowing only a very small percentage, it is especially important that this constituent should be accurately determined.

Quantity No. 2—Determination of Total Sulphur.—Two methods are available—(a) by oxidation with nitric acid or other liquid oxidising reagents, or (b) by fusing with an oxidising fusion mixture, the sulphur in each case being converted into sulphuric acid.

(a) *By Oxidation in the Wet Way.*—A little water and dilute hydrochloric acid are added to the weighed quantity in flask to expel carbon dioxide. As small a quantity as possible should be used. Strong fuming nitric acid is then added, and the flask is gently heated on a water-bath, a small funnel being placed in the mouth to avoid loss by spitting. A little powdered chlorate of potash is added in small portions. When the oxidation is judged to be complete, the contents of flask are washed out into a porcelain dish, a little chloride of sodium is added, and the contents of the dish are evaporated to dryness. When cold, a little strong hydrochloric acid is added, and the solution is again evaporated to dryness. The nitric acid is replaced by hydrochloric acid by repeating this operation once or twice, and the residue is finally taken up with hydrochloric acid as in the separation of silica. Water is added, and the precipitate is filtered off. The filtrate is boiled, a little boiling solution of barium chloride added, and the boiling is continued for several minutes. The beaker is set aside for a few hours, the precipitate is then filtered off, washed, dried, ignited, and weighed.

(b) The weighed quantity in the platinum crucible is mixed with a little fusion mixture, composed of four parts of sodium carbonate to one part of potassium nitrate, by carefully stirring with a rounded glass rod,

and is fused at a gentle heat. This fusion is best done with a Berzelius spirit lamp, or a Swedish lamp. If coal gas is used, care must be taken that the contents of the crucible are not contaminated with sulphur from the flame. The lower part of the crucible should be inserted into a hole cut in a piece of asbestos millboard, which it should accurately fit. When cold, the melt is boiled out with water, and evaporated to complete dryness, after the addition of hydrochloric acid. The residue is taken up with hydrochloric acid and water, and the precipitate filtered off. The sulphuric acid is determined in the filtrate exactly as in 1.

Quantity No. 3—Sulphur occurring as Sulphuric Acid.—The quantity in the beaker is treated with a little water and dilute hydrochloric acid, and is heated to expel carbon dioxide. The precipitate is filtered off, washed, and the sulphuric acid is determined in the filtrate in the manner previously described. The sulphuric acid found here exists most probably in combination with lime as calcium sulphate, and to this it is usually calculated. The percentage of sulphuric acid found here is deducted from the percentage found in the quantity taken for total sulphur. From the difference, the sulphur present as sulphide is calculated to ferric sulphide, FeS_2 . Care should be taken that the reagents used for these determinations are themselves free from sulphur.

Quantity No. 4—Determination of the Alkali Metals.—These are best determined by Professor Laurence Smith's method, of which we give a brief summary. Full details will be found in Crookes' *Select Methods in Chemical Analysis*.

The silicate is fused with its own weight of pure ammonium chloride and six times its weight of pure calcium carbonate, prepared by precipitation with ammonium carbonate from a hot solution of the pure chloride, the precipitated calcium carbonate being filtered off, well washed, and dried.

It must be remembered that the silicate forms only a portion of the materials, the analyses of which we are considering, and that a considerable quantity of calcium carbonate is already present. This fact should be taken into account when calculating the quantities of ammonium chloride and calcium carbonate to be added. Thus in a cement mixture containing, as it would do, about 75 per cent. of carbonate of lime, it would only be necessary to add ammonium chloride to the extent approximately of one-quarter the weight of the substance taken, and calcium carbonate equal to three-fourths of its weight.

The required quantities of ammonium chloride and calcium carbonate having been weighed off, they are intimately mixed in a small mortar, and added to the weighed quantity of the substance in the crucible, the contents of which are thoroughly mixed by stirring with a small glass rod or spatula. The mixture is then heated, at first gently, and finally

to full redness for an hour over a blowpipe flame. When cool, the crucible with its contents is placed in a platinum or porcelain dish, water is added, and the contents of dish are heated. The sintered mass, after a time, becomes detached from the crucible and disintegrates. The contents of the crucible are then washed into the dish. When completely disintegrated, the contents of the dish are filtered, and the precipitate is well washed. The precipitate is rejected, the filtrate contains the alkalies, together with lime and also magnesia, if present, as it almost universally is in limestone. The liquid is heated, after ammonium hydrate and ammonium carbonate are added in slight excess, together with a few drops of ammonium oxalate, and it is then filtered. The filtrate and washings are concentrated in a porcelain beaker or large porcelain dish until ammonium salts begin to crystallise out. The contents of the dish are then washed into a wide-mouthed flask of ample capacity, and strong, pure nitric acid is added in sufficient quantity to decompose the ammonium salts present. The flask is heated until the reaction is at an end, and the contents are evaporated upon a sand-bath to complete dryness. Professor Smith proposes as an alternative course to effect the evaporation in a porcelain dish, after the decomposition in the flask is complete; stating that the dish should be of Berlin porcelain. Our own experience is that unless it is of extremely good porcelain, the dish is acted upon to a considerable extent by the acid solution. The residue is boiled with baryta water to remove magnesia, and filtered, the excess of baryta being removed from the filtrate by heating with ammonium hydrate and carbonate. The precipitate is filtered off, and the filtrate is evaporated to complete dryness, after the addition of a few drops of dilute hydrochloric acid in a weighed platinum dish. The dish is carefully heated in a sand-bath to ensure perfect dryness, and when cold it is weighed. The mixed chlorides are separated as follows:—

Separation of the Chlorides.—The contents of the dish are dissolved in water, a few drops of hydrochloric acid are added, together with platinum chloride in excess. The dish is heated on the water-bath until the contents are in a semi-fluid pasty condition, a little alcohol is then added, and the dish is gently shaken to mix the contents. The double salt of platinum and potassium, K_2PtCl_6 , crystallises out as the liquid concentrates on the water-bath. If the liquid becomes colourless, or of a very pale straw colour, sufficient platinum chloride solution has not been added. When the precipitate has settled, the supernatant liquid is decanted off and passed through a filter that has been previously washed, dried at $100^\circ C.$, and weighed. The treatment with alcohol is repeated once. The precipitate is then washed from the dish upon the filter with a jet of alcohol, contained in a small wash-bottle, the washing being continued until the washings are colourless. The paper with the precipitate is

dried at 100° C., and weighed. The sodium chloride is taken by difference. Both chlorides are calculated to oxides.

Quantity No. 5—Determination of Carbon Dioxide.—This should be determined by the increase in weight of absorption tubes, and one of the best forms of apparatus for this purpose is that given by Fresenius,* which may be referred to. We ourselves use this apparatus, and find it to give extremely accurate results. One improvement may be suggested. Instead of the U tubes fitted with corks or caoutchouc stoppers employed by Fresenius, it will be found much more convenient to use those with glass stoppers and leading tubes.

Examination of the Silica Insoluble in a Boiling Solution of Carbonate of Soda.—This may consist entirely of silica, or of silica with some undecomposed silicate. For accurate work its nature should always be determined. Two methods are available:—

1. After weighing, six times its weight of fusion mixture is added to the precipitate in the platinum crucible, and it is then thoroughly mixed with it by stirring with a rounded glass rod. The crucible is heated over a blast-lamp, at first cautiously, finally at full heat, and this heating is continued until all action ceases and the contents remain in a state of calm fusion. The fused substance is treated with dilute hydrochloric acid, heated gently to expel carbon dioxide, and the silica is determined exactly as previously described. Bases, if present—that is, if the silica was not pure quartz sand—are determined in the filtrate.

2. The precipitate is cautiously heated in the platinum crucible, with a little pure hydrofluoric acid and a few drops of sulphuric acid, and evaporated to dryness. This treatment is repeated, the crucible ignited and weighed, and the silica estimated as loss. The residue contains the bases as sulphates. The hydrofluoric acid must be pure, and the operation must be entirely conducted in the open air, or the windows and all glass apparatus in the laboratory will be attacked. Fresenius suggests the use of fluoride of ammonium instead of hydrofluoric acid, but we have not ourselves tried this reagent.

The Analysis of Clay and Shale.

General Classification.—For the purpose of analysis, we may divide clay and shale into three classes:—

1. That in which calcium carbonate is absent, or in which it occurs only in moderate quantity, up to, say, 5 or 6 per cent.
2. That in which calcium carbonate is present in quantities as large as from 20 to 70 per cent., as, for instance, in gault clay, the clays and shales of the lias, and the shales of the carboniferous limestone formation.

* *Quantitative Analysis*, vol. i., p. 340.

3. Alluvial mud from the banks of tidal rivers, such as Medway mud, in which calcium carbonate is either absent or present only in small quantity, but which may contain chlorides and sulphates of magnesium, and of the alkali metals.

1. Analysis of Clay or Shale Containing Calcium Carbonate in Small Quantity.

Initial Preparation.—The sample in the rough state is dried for some time in the steam oven. It is then finely powdered, further dried in the steam oven for several hours, and preserved in a well-stoppered glass tube.

Potash, soda, ferric sulphide, calcium sulphate, and carbon dioxide are determined exactly as in the analysis of limestone.

Determination of Silica, Oxide of Iron, Alumina, Lime, and Magnesia.—From 0.5 to 0.8 gramme is weighed into a platinum crucible, and fused with six times its weight of fusion mixture. Some text-books advise the use of a larger amount than this, which is doubtless necessary for certain silicates, but our own experience shows that any of those occurring in cement materials are entirely decomposed by fusion with this quantity, and it is always advisable to introduce as little foreign matter as possible into the substance under examination. The contents of the crucible are fused, the fused mass is treated with dilute hydrochloric acid, heated to expel carbon dioxide, and evaporated to dryness in a platinum dish. The silica, oxide of iron, alumina, lime, and magnesia are determined as in limestone, except that the magnesia is precipitated in the filtrate from the lime—being concentrated if necessary—without removal of the ammonium salts.

Sand may be determined as follows:—About 0.5 gramme of the dry clay is weighed from the tube and transferred to a platinum dish. Sulphuric acid, diluted with its own volume of water, is added, the contents of the dish are strongly heated for about nine hours, then evaporated nearly to dryness, and boiled with water. The sand and the silica which was previously combined with bases are filtered off and well washed with hot water. The matter is washed out of the filter into the platinum dish; the sand is then separated, and its nature is determined exactly as in the case of limestone.

Determination of Combined Water and Organic Matter.—Two sufficiently accurate methods are available according to circumstances, viz.:—

(a) A weighed quantity, from 0.5 to 1 gramme, of the clay, after drying in the steam oven, is ignited over a blast-lamp until the weight is constant. If ferric sulphide and calcium carbonate are absent, the loss may be set down as water and organic matter. If ferric sulphide is present, the loss consists of water, organic matter, and sulphur, the latter being replaced by oxygen; the iron, previously in combination with it,

existing now as ferric oxide. The loss per cent. on ignition requires, therefore, to be diminished by the percentage of ferric sulphide in the clay, and increased by the equivalent quantity of ferric oxide. If calcium carbonate is present, the percentage of carbon dioxide must of course be deducted from the total percentage of loss. If ferric sulphide and calcium carbonate are both present, the method (b) should be adopted in preference.

(b) From 0.5 to 1 gramme of the dried clay is treated in a beaker or evaporating dish with water and very dilute hydrochloric acid in very slight excess, warmed gently to expel carbon dioxide, rendered slightly alkaline with ammonium hydrate, heated to boiling, and filtered through an ashless filter paper, which has been previously dried in the steam oven, and weighed. The residue on the filter is well washed, dried with the filter paper in the steam oven for two hours, and again weighed. From the loss of weight after ignition, less the weight of filter paper, the loss per cent. is calculated. This should be corrected for ferric sulphide, as described under method (a).

2. Analysis of Clay or Shale Containing Calcium Carbonate in Considerable Quantity.

Preparation.—The sample is prepared for analysis as in 1.

Determination of Potash and Soda, Ferric Sulphide, Calcium Sulphate, and Carbon Dioxide.—These are determined exactly as in limestone in separate portions of the dry clay.

Combined Water and Organic Matter.—About 1 gramme of the dried clay is weighed, transferred to a beaker or evaporating dish, water is added, and then dilute hydrochloric acid, in very slight excess; the mixture is heated to expel carbon dioxide, ammonium hydrate is added in very slight excess, the whole heated to boiling, filtered through a dried and weighed filter paper, well washed, dried in the steam oven for two hours, and weighed. The weight, less that of the filter paper, is that of the actual clay in the quantity taken. It is strongly ignited with the filter paper in a platinum crucible, and again weighed. Its weight, deducted from that previously found, less that of the filter paper, is that of the combined water and organic matter, which should be corrected if ferric sulphide is present.

Lime and Magnesia as Carbonates.—These are determined in the filtrate from the clay exactly as in limestone.

Silica, Oxide of Iron, Alumina, Lime, and Magnesia as Silicates.—The clay, after ignition, is fused in the platinum crucible, and these constituents are determined exactly as in the first method for clay.

Sand.—This is determined in about 1 gramme of the original clay by the method previously described.

3. Analysis of Medway or Salt Water Mud.

This may be analysed by the first method given for clay. The analysis of Gillingham mud, given in the next chapter, was made by the following method, which may be employed if a more detailed examination is required :—

Preparation.—This material is prepared for analysis as in the previous instances.

About 8 grammes of the dried clay are weighed off, digested with water, treated with a few drops of dilute nitric acid, filtered through a weighed filter paper, well washed, dried in the steam oven, and weighed. The filtrate is made up to one litre.

The clay is separated from the filter paper, finely powdered, and preserved in a tube. Sand, silica, oxide of iron, alumina, lime, magnesia, ferric sulphide, potash, soda water, and organic matter are estimated in portions of this, as in the case of No. 2. Carbon dioxide, if present, is determined in a portion of the original clay.

250 c.c. of the filtrate from the clay are taken for the determination of silica, oxide of iron, alumina, lime, and magnesia.

250 c.c. are taken for the determination of the alkali metals. The quantity is transferred to a beaker, rendered alkaline with ammonium hydrate, heated to boiling, ammonium carbonate is added to separate any lime present, and the solution is filtered. The filtrate is evaporated to dryness in a platinum dish, and the ammonium salts are removed by gentle ignition. The residue is boiled with a little baryta water, filtered, the excess of baryta being separated from the filtrate with ammonium hydrate and ammonium carbonate, again filtered, and the filtrate evaporated to complete dryness in a weighed platinum dish. After being weighed, the mixed chlorides are evaporated with platinum chloride, as described in the analysis of limestone. Sulphuric acid is determined in 200 c.c. of the solution. 200 c.c. are rendered neutral or very faintly alkaline with sodium carbonate, a few drops of potassium chromate solution are added, and the chlorine is determined by titration with standard silver nitrate.

The Analysis of Portland Cement.

Determination of Silica, Oxide of Iron, Alumina, Lime, and Magnesia.—These are determined exactly as in the case of limestone or the mixture of raw materials, in from 0.5 to 0.8 gramme of the finely-powdered cement. Previous ignition is not necessary, as the silica separates entirely as a gelatinous hydrate on heating and digesting the cement with hydrochloric acid. Before adding this acid the weighed quantity should be triturated with a little water until all tendency to set has disappeared. The iron may, if preferred, be determined in a separate portion of the

cement, by which means the troublesome bisulphate of potash fusion of the mixed oxides is avoided. From 1 to 2 grammes of the cement are weighed off, boiled with dilute hydrochloric acid until decomposed, the solution reduced, and titrated with standard bichromate. Or the hydrochloric acid solution is rendered slightly alkaline with ammonium hydrate, boiled, the precipitate filtered off, washed out of the filter, and dissolved in dilute sulphuric acid. The solution is reduced by zinc or hydrogen sulphide, and the iron is determined by titration with permanganate. If hydrogen sulphide is employed for the reduction the excess is boiled off while passing carbon dioxide through the flask.

Determination of Ferrous Iron.—A weighed quantity of from 4 to 5 grammes of cement is triturated with excess of water in an evaporating dish until all tendency to set has ceased, when a little bicarbonate of soda is added. The mixture is washed into a flask with a double-bored stopper, through one hole of which passes a funnel or thistle-headed tube with stopcock, through the other a tube fitted with a Bunsen valve. The cement is decomposed by heating with hydrochloric acid, which is admitted to the flask by the funnel tube, and the ferrous iron is determined by titration with standard bichromate.

Determination of Insoluble Silica and Sulphuric Acid.—In all cements a portion of the silica is insoluble in a boiling solution of sodium carbonate, and is, consequently, inactive. In analysis results such silica is frequently described as "insoluble residue," and in cements of good quality it rarely exceeds from 1 to 2 per cent. A weighed quantity of about 1 gramme of the cement under examination is decomposed by hydrochloric acid in a porcelain or platinum dish, evaporated to dryness on the water-bath, the silica separated and filtered off, and the sulphuric acid determined in the filtrate by precipitation with barium chloride, as previously described. The evaporation to dryness is not absolutely necessary, but the time occupied is saved by the more ready filtration. The silica is washed out of the filter into a platinum dish, and the insoluble portion is determined by boiling with solution of carbonate of soda. The percentage found is deducted from that of the total silica.

Determination of Sulphide Sulphur.—About 5 grammes are taken for the determination of sulphur existing, combined with calcium, as calcium sulphide. The weighed quantity is triturated in a porcelain dish with water to a thin slip until it shows no further tendency to set. It is washed into a flask fitted with a doubly-bored rubber cork. A funnel tube passes through one of the holes, and reaches nearly to the bottom of the flask; one limb of a tube bent twice at right angles is inserted in the other hole, reaching only just through the cork. The other limb dips into a solution of cadmium chloride contained in a beaker or a tall narrow cylinder. It should reach nearly to the bottom of the vessel. Hydro-

chloric acid is passed through the funnel into the flask, which is gently heated until the cement is entirely decomposed, the contents being finally boiled. The contents of the beaker are passed through a filter that has been previously washed, dried at 100°C ., and weighed. The precipitate is well washed and dried with the filter at 100°C ., the percentage of calcium sulphide being calculated from the weight of the cadmium sulphide.

Potash and Soda.—These are determined by Lawrence Smith's method, as before.

Determination of Carbon Dioxide and Water.—A weighed quantity of about 0.5 gramme is strongly ignited in a platinum crucible to constant weight. The loss, generally described in analysis results as "loss on ignition," is considered to be carbon dioxide and water. Carbon dioxide alone may be determined by the apparatus devised by Dr. Fresenius, previously referred to. From 4 to 5 grammes should be taken for the determination, which should be triturated with water before being transferred to the evolution flask. By a modification of this apparatus, as used for the analysis of black ash,* both carbon dioxide and sulphur existing as sulphide may be determined at one and the same operation.

The Analysis of Lime.

Hydraulic lime may conveniently be analysed by the method given for Portland cement. With comparatively pure limes the method selected must depend upon what is required to be known regarding them. Frequently a determination of lime alone, or of lime and magnesia, is all that is needed. A weighed quantity of about 0.5 gramme is dissolved in hydrochloric acid, the solution is rendered slightly alkaline with ammonium hydrate, boiled, and the precipitate of silica, oxide of iron, and alumina filtered off, dried, ignited, and weighed. Lime and magnesia may be determined in the filtrate. The loss on ignition should not be neglected in any analysis of lime. By determining also the carbon dioxide, the actual lime and that present as carbonate and as hydrate may be stated in the results. If it is required to determine the silica, oxide of iron, and alumina, about 2 grammes should be taken for the analysis, and these constituents may be separated as in Portland cement. The filtrate from the oxide of iron and alumina is made up to 1 litre; 250 c.c. are taken for the determination of lime and magnesia, and 500 c.c. for sulphuric acid.

Notes.—In many cases it will not be necessary to completely analyse cement or cement materials. An accurate determination of some of the principal constituents is frequently all that is required. A double evaporation to separate silica should always be made, as also a double precipitation of the oxide of iron and alumina, if lime and magnesia are present. It should also be remembered that a single precipitation effects only a very imperfect separation of magnesia from lime. The determination of carbon dioxide is often omitted, as it is assumed that the whole of

* Fresenius, *Quantitative Analysis*, vol. ii., p. 234.

the lime and magnesia is present as carbonate. This is not strictly true, as a portion of these substances, although often a small one, exists as silicate, especially in hydraulic limestones. Further reference to this will be made in the following chapter when dealing with rapid methods of determining carbonate of lime in raw materials and mixtures. In some materials sulphur in any form occurs in such small quantity that for practical purposes its presence may be disregarded. When dealing with lias materials it must not be ignored, as some of the beds contain iron pyrites in such quantities as to unfit them for the purpose of cement manufacture. The same may be said of many of the carboniferous limestone shales, while gault clay frequently contains notable amounts of selenite. A perfect method of cement analysis has yet to be devised. In the present state of our knowledge we can only make an ultimate analysis, and determine the percentage of each constituent. They undoubtedly exist in combination, but no method of proximate analysis by which these compounds may be separated and determined is as yet known.

Taken alone, the analysis of Portland cement is no indication of its quality. It may agree in ultimate composition with cement that has been proved to be of the highest quality, and yet itself be faulty. Chemical analysis will show if it has been made from suitable materials, if they have been combined in the correct proportions, and if certain constituents—such as magnesia and sulphuric acid, an excess of which would be likely to give trouble—are within the proper or the required limits. It is also possible by this means to detect most forms of adulteration. The analysis will not show if the constituents of the raw mixture, although in the correct proportions, have been properly ground or uniformly mixed, or even if the cement has been sufficiently burned. To determine these points, and to obtain complete information as to the properties of Portland cement, recourse must be had to mechanical tests, in addition to chemical analysis.

Cement Adulteration.

Detection of Adulteration.—The admixture of Portland cement with less valuable materials is not commonly practised in this country. Attention was first called to the subject about nine years ago, when certain manufacturers in the London district were found to be grinding Kentish rag—a siliceous limestone—with their clinker. The practice in question is, however, of much older date than this. So far back as 1871, John Glover, the inventor of the Glover Tower, so well known in the alkali industry, read a paper before the Chemical Society of Newcastle-upon-Tyne “on the adulteration of Portland Cement with slags.” In 1882, attention was called to the subject at a meeting of the German Society of Cement Manufacturers, and it was declared to be a fraud upon the purchaser. Experiments were undertaken by Messrs. R. & W. Fresenius at the request of the Society,* and certain rules for its detection were laid down. The subject was investigated in this country by Messrs. Stanger & Blount, with special reference to the addition of Kentish rag.

The choice of materials for this purpose is necessarily limited, as they must be of low cost, and they must not affect the colour of the cement.

* *Zeitschrift für analytische Chemie*, vol. xxiii., p. 175.

Among possible ingredients are certain limestones, sandstones, old fire-bricks, hard shales, and blast-furnace slag. The addition of sandstone, siliceous limestone, shale, or firebrick is easily detected by the determination of insoluble residue. This, in a normal cement, does not exceed 2 per cent., and is generally less. If higher than 2 per cent., the addition of some siliceous substance may be taken for granted.

The loss on ignition in well-burned and matured cement rarely exceeds 2.5 per cent. If limestone has been added, it will certainly be greater than this, while the addition of an impure limestone will also result in a high percentage of insoluble residue.

Adulteration by blast-furnace slag is not easily detected, as many slags approach very closely in their composition to that of Portland cement. Owing to the presence of sulphur as sulphide and ferrous iron, Messrs. Fresenius found that the reducing action of slags, when titrated with potassium permanganate, was much greater than that of pure Portland cement. Of 12 samples of pure cements experimented upon, the quantity of permanganate, reduced by 0.1 gramme, varied from 0.79 to 2.8 milligrammes; of 5 samples of slag, from 44.34 to 74.6 milligrammes. From these results they say that the weight of permanganate, reduced by 1 gramme of cement, should not exceed 2.8 milligrammes. This is disputed by Dr. Michaelis,* who experimented with 5 samples of pure cement. No. 1 required 11.6, No. 2 3.3, No. 3 19.9, No. 4 14.7, and No. 5 1.2 milligrammes of permanganate. The Fresenius test would condemn all these except the last.

SYMBOLS AND ATOMIC WEIGHTS OF THE MOST IMPORTANT ELEMENTS.

From the Table of International Atomic Weights.

		O = 16.	H = 1.			O = 16	H = 1
Aluminium, . .	Al	27.1	26.9	Lead,	Pb	206.9	205.35
Antimony, . .	Sb	120.2	119.3	Lithium, . . .	Li	7.03	6.98
Arsenic, . . .	As	75.0	74.4	Magnesium, .	Mg	24.36	24.18
Barium, . . .	Ba	137.4	136.4	Manganese, . .	Mn	55.0	54.6
Bismuth, . . .	Bi	208.5	206.9	Mercury, . . .	Hg	200.0	198.5
Boron,	B	11	10.9	Nickel,	Ni	58.7	58.3
Bromine, . . .	Br	79.96	79.36	Nitrogen, . . .	N	14.04	13.93
Cadmium, . . .	Cd	112.4	111.6	Oxygen,	O	16.00	15.88
Calcium, . . .	Ca	40.1	39.8	Phosphorus, .	P	31.0	30.77
Carbon,	C	12.00	11.91	Platinum, . . .	Pt	194.8	193.3
Chlorine, . . .	Cl	35.45	35.18	Potassium, . .	K	39.15	38.86
Chromium, . . .	Cr	52.1	51.7	Silicon,	Si	28.4	28.2
Cobalt,	Co	59.0	58.56	Silver,	Ag	107.93	107.12
Copper,	Cu	63.6	63.1	Sodium,	Na	23.05	22.88
Fluorine, . . .	F	19	18.9	Strontium, . . .	Sr	87.6	86.94
Gold,	Au	197.2	195.7	Sulphur,	S	32.06	31.83
Hydrogen, . . .	H	1.008	1.000	Tin,	Sn	119.0	118.1
Iodine,	I	126.85	125.90	Titanium, . . .	Ti	48.1	47.7
Iron,	Fe	55.9	55.5	Zinc,	Zn	65.4	64.9

* *Thonind. Zeit.*, vol. xxiv. (59), p. 860.

FACTORS FOR USE IN CEMENT ANALYSIS WITH THEIR LOGARITHMS.
Calculated from the Atomic Weights in the International Table—H=1.

Found.	Sought.	Factor.	Logarithm.
BaSO ₄	CaSO ₄	·5831	$\overline{1}$ ·7657430
BaSO ₄	CaSO ₄ ·2H ₂ O	·7374	$\overline{1}$ ·8677031
BaSO ₄	S	·1373	$\overline{1}$ ·1376705
BaSO ₄	SO ₃	·3429	$\overline{1}$ ·5351675
BaSO ₄	H ₂ SO ₄	·4206	$\overline{1}$ ·6238693
2BaSO ₄	FeS ₂	·2570	$\overline{1}$ ·4099331
CdS	CaS	·4994	$\overline{1}$ ·6984485
CdS	S	·2219	$\overline{1}$ ·3461573
CdS	CaSO ₄	·9422	$\overline{1}$ ·9741431
CaO	CaCO ₃	1·7843	0·2514679
CaO	CaSO ₄	2·4272	0·3851056
CaO	CaSO ₄ ·2H ₂ O	3·0695	0·4860676
CaO	CaOH ₂ O	1·3211	0·1209357
CaCO ₃	CaO	·5604	$\overline{1}$ ·7484981
CaCO ₃	CaSO ₄	1·3603	0·1336347
CaCO ₃	CaSO ₄ ·2H ₂ O	1·7202	0·2355789
CaCO ₃	CO ₂	·4395	$\overline{1}$ ·6429589
CO ₂	CaCO ₃	2·2750	0·3569814
CaSO ₄	CaSO ₄ ·2H ₂ O	1·2645	0·1019188
CaSO ₄	SO ₃	·5880	$\overline{1}$ ·7693773
SO ₃	CaSO ₄	1·7006	0·2306022
CaOH ₂ O	CaO	·7569	$\overline{1}$ ·8790385
Fe ₂ O ₃	2FeO	·8999	$\overline{1}$ ·9541943
2FeO	Fe ₂ O ₃	1·1112	0·0457922
Fe ₂ O ₃	2FeS ₂	1·5022	0·1767278
FeS ₂	Fe ₂ O ₃	·6656	$\overline{1}$ ·8232133
FeS ₂	Fe	·4657	$\overline{1}$ ·6681062
FeS ₂	S ₂	·5342	$\overline{1}$ ·7277039
MgO	MgCO ₃	2·0901	0·3201671
MgCO ₃	MgO	·4784	$\overline{1}$ ·6797912
Mg ₃ P ₂ O ₇	2MgO	·3624	$\overline{1}$ ·5591882
Mg ₃ P ₂ O ₇	2MgCO ₃	·7575	$\overline{1}$ ·8793826
K ₂ PtCl ₆	2KCl	·3071	$\overline{1}$ ·4872798
K ₂ PtCl ₆	K ₂ O	·1941	$\overline{1}$ ·2890255
2KCl	K ₂ O	·6320	$\overline{1}$ ·8007171
2NaCl	Na ₂ O	·5308	$\overline{1}$ ·7249309

CHAPTER VII.

ANALYSES OF RAW MATERIALS AND PORTLAND CEMENT,
CALCULATIONS OF PROPORTIONS, RAPID METHODS OF
MAKING DETERMINATIONS, AND SPECIFIC GRAVITY.

CONTENTS.—Analyses of Raw Materials, Portland Cement, and Clinker—Calculations of Proportions of Lime and Clay—Rapid Methods of Testing—Calcimeter and Nitrometer—Direct Determination of Lime in Raw Mixtures—Specific Gravity.

Analyses of Raw Materials.—The analyses which follow have been selected from among others made by the authors as being fairly representative of materials either generally employed in, or suitable for, the manufacture of Portland cement. In the clays and shales the uncombined silica has not, in every case, been determined, as modern practice conclusively shows that, if the mixture with carbonate of lime is suitably proportioned and ground sufficiently fine, sandy clays, or those in which much of the silica occurs in the free state, may be successfully used, the whole of the silica being brought into the soluble form during the process of burning. Analyses of lias limestones have been given in an earlier section of the book.

GAULT CLAY.

No. 1 from Arlessey, Herts; No. 2 from Sussex.

	No. 1.	No. 2.
Silica (as fine sand),	12·28	16·35
Silica, combined,	27·53	28·08
Oxide of iron,	5·70	7·47
Alumina,	13·94	15·08
Lime,	1·18	1·08
Magnesia,	1·17	·90
Carbonate of lime,	30·73	21·52
Carbonate of magnesia,	1·38	1·10
Sulphate of lime,	·52	1·96
Combined water and organic matter,	5·02	5·80
Potash and soda (not determined),	...	...
	99·45	99·34

CALCAREOUS CEMENTS.

MEDWAY MUD.

From Gillingham.

Silica,	38.413	} As sand in an extremely fine state of division.
Alumina, with trace of iron,	1.856	
Silica,	25.249	} Combined as silicate.
Alumina,	14.244	
Oxide of iron,	6.774	
Lime,	.810	
Magnesia,	1.727	
Potash,	2.957	
Soda,	.773	
Water,	3.384	
Iron pyrites,	.214	
Silica,	.118	
Oxide of iron, with trace of oxide of manganese,	.214	
Alumina,	.123	
Calcium sulphate,	.490	
Magnesium sulphate,	.425	
Magnesium chloride,	.024	
Potassium chloride,	.524	
Sodium chloride,	2.166	
	100.455	

ALLUVIAL CLAY.

North of England.

Silica (as fine sand),	41.84
Silica, combined,	24.22
Oxide of iron,	6.80
Alumina,	15.00
Lime,	1.66
Magnesia,	1.43
Sulphate of lime,	.19
Combined water and organic matter,	7.95
Potash and soda (not determined),	...
	99.09

BOULDER CLAY.

From the Tyne.

Silica (as fine sand),	14.56
Silica, combined,	41.43
Oxide of iron,	10.66
Alumina,	15.81
Lime,	3.00
Magnesia,	2.16
Sulphate of lime,	.15
Combined water and organic matter,	10.64
Potash and soda (not determined),	...
	98.41

S H A L E S .

No. 1, Carboniferous, South of Ireland ; No. 2, Silurian, South of Ireland.

	No. 1.	No. 2.
Silica,	64·05	69·00
Oxide of iron,	8·04	8·50
Alumina,	16·06	16·07
Lime,	1·00	·35
Magnesia,	1·58	2·15
Potash,	3·44	*
Soda,	1·61	*
Loss on ignition,	4·29	3·07
	100·07	99·14

* Not Determined.

CHALK AND LIMESTONE.

No. 1. Upper or white chalk,	Kent, England.
„ 2. Lower or grey chalk,	„
„ 3. „ „ „ „ „ „ „ „ „	„
„ 4. Carboniferous limestone,	Kilkenny, Ireland.
„ 5. „ „ „ „ „ „ „ „ „	Charlestown, Scotland.
„ 6. „ „ „ „ „ „ „ „ „	„
„ 7. „ „ „ „ „ „ „ „ „	Lancashire, England.
„ 8. „ „ „ „ „ „ „ „ „	„
„ 9. Cement rock,	Lehigh Valley, Pennsylvania, U.S.A.

RESULTS OF ANALYSES OF CHALK AND LIMESTONE.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.	No. 8.	No. 9.
Silica,	·84	3·43	7·98	·93	7·70	2·15	2·27	1·25	15·28
Alumina,	·23	1·73	2·86	·25	1·23	·27	1·46	·32	4·50
Oxide of iron,	·09	1·02	1·31	·32	1·65	·42	·79	·21	1·61
Iron pyrites,	...	...	...	...	...	...	...	·13	...
Sulphate of lime,	...	...	...	...	...	...	·23	...	...
Carbonate of lime,	98·37	92·98	86·45	97·87	87·36	95·97	93·47	95·04	71·21
Carbonate of magnesia,	·21	·49	·64	·45	1·92	1·41	1·42	2·54	5·67
	99·74	99·65	99·24	99·82	99·86	100·22	99·64	99·49	98·27

RAW CEMENT MIXTURES.

No. 1. From white chalk and Medway mud.
„ 2. „ grey chalk and gault clay.
„ 3. „ blue lias limestone and clay.
„ 4. „ carboniferous limestone and clay.
„ 5. „ calp limestone and shale, Dublin ; and limestone from Kildare.
„ 6. „ hard crystalline limestone and white clay, New South Wales.
„ 7. „ lower carboniferous limestone, limestone shale, and fresh-water river alluvium.

All these, except the first two, are dry process mixtures.

RESULTS OF ANALYSES OF RAW CEMENT MIXTURES.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.
† Insoluble siliceous matter,	6.57	2.50	2.58	5.57	12.21	7.18	7.49
Silica,	7.63	11.83	11.41	9.61	2.74	8.49	7.15
Alumina,	4.32	5.23	4.80	3.45	3.06	3.90	3.69
Oxide of iron,	1.89	1.97	2.34	2.42	1.87	2.01	1.88
Iron pyrites,	.27	...	.43	...	.95	...	†
Carbonate of lime,	75.39	74.18	74.09	75.89	75.01	76.24	75.46
Carbonate of magnesia,	1.54	1.29	2.61	1.50	2.34	1.06	3.19
Sulphate of lime,	.17	.18	.21	.16	†	...	.08
Potash,	*	.31	.83	.88	†	.84	*
Soda,	*	.31	.46	.39	†	.15	*
Combined water,	1.42	1.82	.43	.61	.71	1.79	.50
	99.20	100.21	100.29	100.48	98.99	100.66	99.14
† Consisting of—							
Silica,	5.83	2.27	2.27	5.03	10.77	6.57	6.56
Alumina with trace of iron,	.49	.23	.31	.54	.96	.56	.55
Lime,	.21	...	...	...	.30	...	...
	6.53	2.50	2.58	5.57	12.03	7.13	7.11

* Not determined.

† Trace.

PORTLAND CEMENT.

- No. 1. From white chalk and Medway mud.
 „ 2. „ grey chalk and gault clay.
 „ 3. „ blue lias limestone and clay.
 „ 4. „ chalk marl and alluvial clay.
 „ 5. „ white chalk and boulder clay.
 „ 6. „ carboniferous limestone, shale, and alluvial clay.
 „ 7. „ „ „ „
 „ 8. „ carboniferous limestone and shale.

RESULTS OF ANALYSES OF VARIOUS SAMPLES OF PORTLAND CEMENT.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.	No. 8.
Insoluble siliceous matter, . . .	2·89	1·23	4·55	1·65	1·35	1·49	1·22	1·40
Silica, . . .	21·30	21·33	16·86	21·79	20·92	20·12	20·70	19·74
Alumina, . . .	6·59	9·17	6·36	6·71	7·46	6·71	6·88	5·97
Oxide of iron, . . .	5·38	4·16	4·83	4·62	4·97	4·03	4·04	4·73
Lime, . . .	61·45	61·06	62·50	61·38	59·63	60·99	63·67	62·88
Magnesia, . . .	·44	1·32	2·36	1·65	1·34	2·29	1·53	2·63
Sulphate of lime, . .	1·42	·80	1·58	·80	1·86	1·89	1·24	1·54
Water and carbonic acid, . . .	...	...	...	...	2·06	1·70	...	·74
Potash, . . .	·43	·73	·97	·89	*	*	*	*
Soda, . . .	·42	·40	·52	·53	*	*	*	*
	100·32	100·20	100·57	100·02	99·159	92·22	99·28	99·63

* Not determined.

ROTARY KILN CLINKER.

No. 1.	From Ransome's kiln. . .	1890.	Dry process.	Fuel, producer gas.
„ 2.	Rüdersdorf, nr. Berlin. . .	1903.	„ „	„ powdered coal.
„ 3.	Thames. . .	1902.	Wet „	„ „
„ 4.	Klagstrop, South Sweden. . .	1903.	„ „	„ „
„ 5.	Thames. . .	1902.	„ „	„ oil.
„ 6.	Sussex. . .	1901.	„ „	„ powdered coal.
„ 7.	Medway. . .	1901.	„ „	„ „
„ 8.	Lehigh Valley, Penn-sylvania. . .	1898.	Dry „	„ „
„ 9.	Thames. . .	1903.	Wet „	„ „
„ 10.	Medway. . .	1903.	„ „	„ „

CALCAREOUS CEMENTS.

ANALYSES OF VARIOUS SAMPLES OF ROTARY KILN CLINKER.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.	No. 8.	No. 9.	No. 10.
Insoluble residue, .	2.36	.25	.48	.19	.21	.29	.45	.35	.56	.49
Silica,	18.43	22.53	23.19	23.46	27.16	23.26	22.49	22.80	25.24	23.31
Oxide of iron, .	4.45	5.95	5.41	3.91	4.42	4.66	5.60	3.75	6.84	4.37
Alumina, . . .	7.23	5.82	8.35	5.68	6.57	7.94	7.34	6.04	5.89	6.28
Lime,	65.44	60.33	59.87	61.74	58.33	61.54	59.66	61.78	58.99	60.99
Sulphate of lime, .	.16	2.82	.92	1.16	.33	.35	.60	2.13	.71	.68
Magnesia, . .	1.91	2.07	1.09	1.70	1.17	.88	1.15	.92	1.37	1.08
Potash, . . .	.07	*	*	*	*	*	*	*	*	*
Soda,	.11	*	*	*	*	*	*	*	*	*
Loss on ignition, .	...	...	.25	.64	1.54	.46	1.56	1.37	.19	2.20
	100.16	99.77	99.56	98.48	99.73	99.38	98.75	99.14	99.79	99.40

* Not determined.

Calculation of Proportion of Raw Materials.—From the results of the analysis of the raw materials, the proportions in which they should be mixed may be calculated. Le Chatelier states that the proportion of lime in Portland cement of good quality should not be greater than that required by the formula :—

$$\frac{\text{CaO} + \text{MgO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3} = 3.$$

or less than that required by :—

$$\frac{\text{CaO} + \text{MgO}}{\text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3} = 3.$$

In both formulas the quantities indicated are equivalents, and not weights. These formulas assume that magnesia is equivalent to, and operates as, lime, an assumption which is not now generally accepted. This is pointed out by Dr. Erdmenger,* who eliminates the magnesia, and writes the formula—

$$\frac{\text{CaO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3} = 3,$$

stating that it may give a product too high in lime, and that many cements of good quality are represented by—

$$\frac{\text{CaO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3} = 2.5.$$

Highly siliceous clays require more lime than those rich in alumina, but by the preceding formulas the lime can only be proportioned to the silica and alumina taken together. Based upon the result of researches, which will be referred to later, Messrs. Newberry represent the composition of Portland cement by the following formula, in which the magnesia is disregarded, and the lime is proportioned to the relative quantities of silica and alumina present :—

$$X (3\text{CaOSiO}_2) + Y (2\text{CaOAl}_2\text{O}_3).$$

3CaOSiO_2 corresponds to 2.8 parts of lime by weight to 1 part of silica, and $2\text{CaOAl}_2\text{O}_3$ represents 1.1 part of lime to 1 of alumina. Substituting weights for equivalents, the formula reads :—

$$\text{Lime} = \text{Silica} \times 2.8 + \text{Alumina} \times 1.1.$$

To illustrate the method of calculating from this formula, we will take a carboniferous limestone and a boulder clay of which the analyses are as follows :—

* *Chem. Zeit.*, 1893, vol. xvii., p. 982.

	Limestone.	Clay.
Silica,	2.06	55.77
Alumina,	.35	17.76
Oxide of iron,	1.32	9.23
Lime,	51.99	4.38
Magnesia,	.66	2.93
Loss on ignition,	43.12	8.96
	99.50	99.03

LIMESTONE.

Per cent. silica,	$2.06 \times 2.8 =$	5.77
„ alumina,	$.35 \times 1.1 =$	.38
		6.15

That is, 6.15 parts of lime are required for the silica and alumina present in limestone, leaving $51.99 - 6.15 = 45.84$ parts available for combination with the silica and alumina in clay.

CLAY.

Per cent. silica,	$55.77 \times 2.8 =$	156.15
„ alumina,	$17.76 \times 1.1 =$	19.53
		175.68
Deduct lime contained in 100 parts clay,		4.38
		171.30

That is, 171.3 parts of lime are required for the silica and alumina contained in the clay. In the limestone 45.84 per cent. of lime is available; therefore, for 100 parts of clay there are required $\frac{171.3 \times 100}{45.84} = 373.6$ parts of limestone. The percentage of carbonate of lime in this mixture is calculated as follows:—

100 parts of clay contain $4.38 \times 1.7843 = 7.81$ parts of carbonate of lime.

100 parts of limestone contain $51.99 \times 1.7843 = 92.76$ parts of carbonate of lime.

373.6 parts of limestone will contain $\frac{92.76 \times 373.6}{100} = 346.5$ parts of carbonate of lime.

The mixture thus consists of—

100	parts of clay containing	7.81	parts of carbonate of lime.
<u>373.6</u>	„ limestone containing	<u>346.50</u>	„ „
473.6	„ mixture containing	354.31	„ „

Carbonate of lime per cent. $\frac{354.31 \times 100}{473.6} = 74.81.$

The proportions of the raw materials are frequently calculated so as to give a desired percentage of carbonate of lime in the mixture. Whatever the composition of the materials, if they are suitable for the manufacture of Portland cement, this percentage will vary between very narrow limits and will lie between 75 to 77 or 77·5 per cent. In most cases from 75 to 76 per cent. will give the best results, except perhaps in the case of very siliceous clays, when the carbonate of lime may reach to 77·5 or even 78 per cent. The relative proportions of the two materials may be determined by the following simple rules:—

1. From the percentage of carbonate of lime contained in the chalk or limestone deduct the percentage required in the mixture, the result will be the weight of clay or shale needed.

2. From the required percentage of carbonate of lime in the mixture deduct the percentage contained in the clay or shale, the result will be the weight of limestone to be used.

For example, let us assume the case of a clay or shale containing 25 per cent. of carbonate of lime and a chalk or limestone containing 91 per cent., both materials being in the dry condition, 76 per cent. of carbonate of lime being required in the mixture. The relative proportions then are—

$$91 - 76 = 15 \text{ parts clay or shale.}$$

$$76 - 25 = 51 \text{ parts chalk or limestone.}$$

$$15 \text{ parts of clay or shale contain } \frac{25 \times 15}{100} = 3\cdot75 \text{ parts of carbonate of lime.}$$

$$51 \text{ parts of chalk or limestone contain } \frac{91 \times 51}{100} = 46\cdot41 \quad \text{,,} \quad \text{,,}$$

$$51 + 15 = 66 \text{ parts of mixture contain } 46\cdot41 + 3\cdot75 = 50\cdot16 \quad \text{,,} \quad \text{,,}$$

$$\text{Carbonate of lime in mixture } \frac{50\cdot16 \times 100}{66} = 76 \text{ per cent.}$$

Obviously, by multiplying each of these proportionate quantities by the same number any convenient weights of the materials may be employed. If the manufacture is by the wet process, allowance must be made for the water present in the materials. In the example given we will assume that these proportions are as follows:—Clay containing 22, and chalk containing 16 per cent. of water in the condition in which they are weighed into the wash-mill. 100 parts of clay then contain 78, and 100 of chalk 84 parts of solid matter.

The relative proportions then are—

$$\text{Clay } \frac{100 \times 15}{78} = 19\cdot23.$$

$$\text{Chalk } \frac{100 \times 51}{84} = 60\cdot71.$$

The composition of the finished cement cannot be accurately cal-

culated from that of the raw mixture, as the results are influenced by the silicates contained in the ash of the fuel. For this reason the results obtained from samples burned in trial kilns cannot successfully be compared with those obtained from the same mixture of materials burned on the manufacturing scale, as in the trial kiln the quantity of fuel required amounts to from twice to three times that necessary in large kilns.

Rapid Methods of Testing the Accuracy of Raw Mixtures, Calcemeters.—The accuracy of the raw mixture requires to be constantly tested, and it is essential that the tests should be rapidly made, so that the proportions, if inaccurate, may be re-adjusted without delay. The result may be arrived at by determining the percentage of loss on ignition of a small quantity—about 0.5 gramme—of the material, previously dried at 100° C., which is strongly ignited in a platinum crucible by a blast-lamp or in a muffle furnace. The result should be compared with that obtained from a normal sample of the same material, the accurate composition of which is known. A weighed quantity may be titrated with a known excess of standard hydrochloric acid, titrating back with alkali agreeing volume for volume with the acid, using methyl orange as an indicator. This is a more rapid method than the one previously described and it involves only one weighing, but in this case, also, the result should be compared with that from a normal sample.

The method most often employed is that of measuring the volume of carbon dioxide evolved upon treating a weighed quantity of the material to be tested with hydrochloric acid, and from this volume calculating the amount of carbonate of lime present. Various special forms of apparatus known as calcimeters have been devised for this purpose, with tables for facilitating or dispensing with calculations. The results from any of them are only approximately accurate, but they are sufficiently so for technical purposes. A portion of the carbon dioxide evolved is retained by the acid employed for the decomposition, and the quantity varies with the volume given off and with the temperature and pressure prevailing at the time the determination is made.

Scheibler's Calcmeter.—An instrument, devised by Dr. Scheibler, for determining the amount of calcium carbonate present in the animal charcoal used for sugar refining, has been frequently employed for making a similar determination in Portland cement mixtures. A description of the apparatus, with instructions for its use, will be found in several text-books of analytical chemistry,* and they need not be repeated here. The principle of its action is this:—The carbon dioxide evolved by the action

* Fresenius, *Chemical Analysis—Quantitative*, vol. i., p. 344, 7th ed.; Sutton's *Volumetric Analysis*, p. 87, 5th ed.; Crooke's *Select Methods in Chemical Analysis*, p. 567, 3rd ed.

of hydrochloric acid upon a weighed quantity of the material to be tested displaces a corresponding volume of water from a graduated tube. To the volume, when read off, is added a correction to allow for the carbon dioxide retained by the acid used for the decomposition. Scheibler gives 0.8 c.c. as the volume to be added to that read off. Warrington * points out that this is not a constant quantity, but is dependent upon the volume evolved, and fixes 7 per cent. of this volume as the quantity to be added. The total volume is reduced to standard conditions, and from this the calcium carbonate is calculated. It has been suggested that, with this apparatus, corrections may be dispensed with by making a determination with pure calcium carbonate—the relation between this amount and that contained in an equal weight of the material tested being a simple proportion statement. For testing cement mixtures it would be better to use as a standard a sample of the same material of which the composition is known. The result of any determination with the standard, of course, only holds good for comparison so long as both temperature and pressure remain unchanged. A second instrument may be employed, and the confined volume may be adjusted as the temperature and pressure alter, but for working in comparison with a standard, Dr. Lunge's nitrometer, the use of which will be presently described, is a much more delicate and convenient instrument.

Dietrich's Calcimeter.—A more modern appliance, and, at the same time, one of the best forms of calcimeter, is that of Dietrich. The measuring tube is graduated into 100 c.c., each of which is subdivided into fifths. This is connected with the levelling tube by thick-walled rubber tubing, the connections being securely bound with wire. Either water or mercury may be used as the confining liquid; the latter is preferable. The tubes are held by clamps attached to a vertical rod which is secured to a cast-iron base plate. An ordinary retort stand answers this purpose sufficiently well. The top of the measuring tube is drawn out to a smaller tube, closed by a short piece of rubber tubing and a pinch cock, a short branch tube is connected with the drawn-out portion, but fixed at right angles to it. The gas generating bottle is of about 150 c.c. capacity, with a wide mouth closed by a rubber stopper, through the centre of which passes a short piece of glass tube. This tube reaches just through the stopper, and is raised sufficiently above it to admit of connection with a rubber tube, which connects the bottle with a coil made of copper or brass pipe of small diameter. This coil is of such a diameter that the generating bottle will easily enter it, and it stands in a tin or copper cylinder containing water. The other end of the coil is connected with the branch on the side of the measuring tube by a sufficient length of rubber tubing, the cylinder with coil and the generat-

* *Chemical News*, vol. xxxi., p. 253.

ing bottle standing on the working bench. The tube for containing the acid is made of gutta percha or vulcanite, and is of such dimensions as to contain 5 c.c. of acid without danger of spilling when leaning at an angle of about 45° in the generating bottle. Either a good aneroid or a Bunsen barometer is necessary, and two thermometers—one for the air, the other for the cylinder containing the coil, the water in which must be maintained at the same temperature as the air. This instrument gives a constant volume for any one sample of material tested, whatever the temperature and pressure; the weight to be taken for the determination consequently varies with the readings of the thermometer and barometer. A table supplied with the apparatus gives the weight for all ordinary temperatures and pressures, and a second table gives the requisite correction for the absorption by the 5 c.c. of hydrochloric acid employed for the decomposition. The weights are so arranged that the indicated volume as read off, plus the number for that volume from the absorption table, gives the percentage of carbonate of lime without further calculation.

Before commencing a determination the height of the barometer and the temperature are noted. These are referred to in the table, and the corresponding weight is ascertained. The required quantity of the dry material is accurately weighed and transferred to the generating bottle. The tube containing 5 c.c. of hydrochloric acid is carefully inserted into the bottle, and is allowed to lean against the side. Commercial hydrochloric acid answers the purpose very well, and is most conveniently measured from a burette, which may be automatically filled from a stock bottle. The pinch cock at the top of the measuring tube is next opened, the stopper is inserted into the bottle, and the level of the confining liquid is carefully adjusted to the zero mark. The pinch cock is then closed, the whole of the acid is brought into contact with the weighed carbonate, by inclining the bottle, using the right hand, the levelling tube being at the same time lowered with the left hand. The bottle is well shaken, placed in the cylinder of water containing the coil, and the levels are roughly adjusted. The bottle will be heated by the hand of the operator, and some heat is also generated by the action of the hydrochloric acid on the carbonate. By the use of the condenser both the bottle and the evolved gas are brought to the temperature of the air. The bottle is from time to time taken from the cylinder, well shaken, and replaced. This is important, as with some materials the liquid retains the carbon dioxide with great obstinacy. Causes contributing to this are the presence of bituminous matter, magnesium carbonate, and silica in the gelatinous state.

When the evolution is complete the bottle is allowed to remain in the condenser, and the tubes are levelled. The volume is read off, and

the correction for absorption is added. The resulting number gives the percentage of carbonate of lime in the sample tested.

Faija's Calcimeter.—The Faija calcimeter is a modified form of the Dietrich apparatus. A pamphlet containing the tables and likewise a full description of the method of using it is supplied with the instrument, but a brief description may be given here. A constant weight of the materials to be tested is taken, the gas volume for any one sample consequently varies with the temperature and pressure. The temperature only need be taken into consideration, as the volume is always measured under the standard pressure of 760 mm. In the arrangement for effecting this, and in the graduation of the measuring tube, the instrument differs from that of Dietrich. The variation in construction is as follows:—The upper end of the levelling tube is drawn out in a similar manner to the lower one, and to this a flexible tube is fastened, which is connected with an aneroid barometer secured to a board which forms the back of the instrument, and to which the tubes are attached. The flexible tube is sufficiently long to admit of the raising and lowering of the levelling tube. A short flexible tube with an india-rubber ball at the end is also connected with the barometer. By a simple piece of mechanism, the barometer may be brought to standard conditions according as the ball is flattened to a greater or less extent between a disc and the board forming the back of instrument. Above the barometer a tap is placed. When this tap is open, the levelling tube is in communication with the outer air; when it is closed it communicates with the barometer. A second tap at the upper end of the measuring tube allows the communication between this and the tube from the generating bottle to be closed. The flexible tube and pinch cock at the top of measuring tube in the Dietrich apparatus is in this type of instrument replaced by a tap. The confining liquid is water. The method of making a determination is the same in both cases, except as regards the final measurement of the gas volume. The weight of material taken is 0.65 gramme, the quantity of hydrochloric acid 10 c.c., and the carbon dioxide is evolved and the tube approximately levelled at the atmospheric pressure. The taps on the measuring tube and above the barometer are then closed, and the barometer is adjusted by compressing or expanding the india-rubber ball until it indicates the standard pressure of 760 mm. The tubes are then accurately levelled, the volume is read off, and the temperature is noted. These numbers are referred to a table which is so arranged that the percentage of carbonate of lime may be at once read off. No correction for absorption is necessary, as this is allowed for in graduating the measuring tube.

Lunge's Nitrometer.—This apparatus may be used for testing raw mixtures. The most suitable form is that with the cup or funnel on the

top of the measuring tube, and fitted with the Greiner-Freidrich tap, mercury being used as the confining liquid. The nitrometer, from its wide applicability, is so well known to all chemists that it need not be described here. To adapt it for the determination of carbon dioxide, a wide-mouthed Erlenmeyer flask, of from 80 to 100 c.c. capacity, is provided, with a well-fitting india-rubber stopper, through which a short piece of glass tube passes. By means of this it is connected with the bent tube from the tap by about 3 inches of strong india-rubber tubing. The acid is contained in a glass or ebonite tube which leans against the side of the flask, and contains 2 c.c. when about half filled. Dr. Lunge uses the nitrometer for the determination of carbon dioxide, taking always 5 c.c. of acid for the decomposition, and calculating the quantity to be added for absorption from the following table by Dietrich:—

TABLE SHOWING THE ABSORPTION OF CARBON DIOXIDE BY 5 C.C. HYDROCHLORIC ACID OF SPECIFIC GRAVITY 1.125.

Given off, c.c., .	1	2	4	6	8	10	12	14	16
Absorbed, c.c., .	1.85	2.00	2.31	2.62	2.93	3.24	3.55	3.86	4.17
Given off, c.c., .	18	20	22	24	26	28	30	32	34
Absorbed, c.c., .	4.48	4.79	4.96	4.98	5.03	5.06	5.09	5.11	5.14
Given off, c.c., .	36	38	40	42	44	46	48	50	55
Absorbed, c.c., .	5.17	5.20	5.23	5.25	5.27	5.30	5.32	5.35	5.41
Given off, c.c., .	60	65	70	75	80	85	90	95	100
Absorbed, c.c., .	5.48	5.55	5.62	5.69	5.76	5.83	5.90	5.97	6.04

The figures found in the second line should be added to those read off in the first line, *before* reducing the volume to 0° and 760 millimetres.

For testing cement mixtures we prefer to work in comparison with a sample of the same material, of which the composition is accurately known, and which is used as a standard. Two similar nitrometers of 50 c.c. capacity are employed. The quantity of material taken is 0.2 gramme. The volume of hydrochloric acid, diluted with its own volume of water, should be 2 c.c. Neither temperature, pressure, nor absorption need be regarded. To make a determination, the taps are turned so that the measuring tube of each instrument communicates with the cup, and the mercury level is adjusted to the zero of the scale. The weighed quantities of the material to be tested and of the standard are transferred to the respective flasks, the tubes with acid are inserted, and the flasks are then attached to the stoppers which always remain on the instruments. Care should be taken to heat them as little as possible by handling. The taps are loosened, and after two or three minutes they are replaced and turned so that the flasks are in communication with the measuring tubes. The acid is then brought into contact with the samples by tilting the

flasks, the levelling tubes are lowered, and the flasks are shaken occasionally until all the gas is evolved. The tubes are levelled, and as soon as the volumes remain constant they are read off. If they agree, the percentage of carbonates in the sample tested is the same as that in the standard; if they do not, a simple proportion sum gives the required result. If only an occasional test is required, one weighing may be saved by providing two small light platinum capsules which exactly balance each other. On one a little of the standard material, equal to about 0.2 gramme, is placed—if desired, this quantity may be approximately weighed—and this amount is used as a weight for the quantity to be tested, which is weighed on the other. For regular work a standard may be set up on commencing, and the volume can be adjusted as the pressure and temperature vary.

Direct Determination of Lime in the Raw Mixture, Lime, and Cement.—This determination is often necessary, and may be made as follows:—Of raw mixture about 0.3 gramme is taken, transferred to a beaker, treated with dilute hydrochloric acid in slight excess, heated to expel carbon dioxide, rendered alkaline with ammonium hydrate, boiled, the solution decanted over a filter, and the precipitate washed twice by decantation. The precipitate is next heated with a little dilute hydrochloric acid, is rendered alkaline with ammonium hydrate, boiled, transferred to filter previously used, and well washed. The lime is determined in the filtrate; the precipitate of clay may, if desired, be ignited and weighed. Of lime and cement about 0.2 gramme is taken, transferred to a beaker, boiled with hydrochloric acid until entirely decomposed, the solution cooled, rendered alkaline with ammonium hydrate, boiled, filtered, and the precipitate washed two or three times on the filter with hot water. The filter is then taken from the stand, and the precipitate is washed out into the beaker in which the precipitation was made, without destroying the paper. It is re-dissolved in hydrochloric acid, rendered alkaline with ammonium hydrate, boiled, filtered, and the precipitate is well washed with hot water. The lime may be determined in the filtrate, and also in that from the clay of raw material as described in the previous chapter, the double precipitation to separate traces of magnesia being omitted, or the clean oxalate precipitate may be dissolved in dilute sulphuric acid, and titrated with $\frac{1}{10}$ normal permanganate. We frequently employ this method, and for technical purposes have found it to give very good results. The filtrate containing the lime is heated to boiling point, boiling solution of ammonium oxalate is added, the boiling of the mixture being continued for a few minutes. The calcium oxalate separates as a granular precipitate, which rapidly settles from the liquid. After standing for about half an hour, the clear liquid is decanted over a 9 cm. filter, and the precipitate is washed by

decantation until it is perfectly clean. This fact may be tested by adding a few drops of calcium chloride solution to the final washings. After boiling and cooling, there should be neither precipitate nor cloudiness. The filter paper is opened out in a flat-bottomed dish of slightly larger diameter, and any adhering precipitate is, as far as possible, washed out into the beaker containing the main quantity. It is then covered with a little dilute 1 : 5 sulphuric acid, warmed, the acid poured into the beaker, and the paper thoroughly washed with hot water, the washings also passing into the beaker. Dilute sulphuric acid is added, the solution is heated to 70° or 80°, and the permanganate solution is cautiously delivered into the liquid with constant agitation until a faint pink colour is permanent. It is a good plan to keep a solution of ammonium oxalate agreeing volume for volume with the permanganate solution for back titration, in case of overrunning. The permanganate solution is standardised in exactly the same manner on pure calcium carbonate.

1 c.c. of $\frac{1}{10}$ normal permanganate = .0028 gramme CaO.
 " " " = .0050 " CaCO₃.

Specific Gravity.—This test should be conducted in the chemical laboratory, as the results obtained by an unskilled operator, even with suitable apparatus, may be very wide of the mark. The determination may be made with the ordinary specific gravity bottle, a liquid without action on cement being substituted for water. Either paraffin or turpentine is generally employed; whichever is used must be absolutely free from water. This may be ensured by shaking the liquid up with finely-ground fresh Portland cement, or by allowing it to stand over freshly-burnt quicklime. If the specific gravity bottle is employed, the specific gravity of the liquid must also be known. This should be determined with a specific gravity bottle, and not with a hydrometer, as is sometimes suggested. If a stock of liquid is kept, it should occasionally be re-determined, especially in the case of turpentine. This method leaves nothing to be desired as regards accuracy, but it is not generally employed, as several forms of apparatus have been devised in which the volume of liquid displaced by a known weight of cement is directly read off, and the specific gravity is calculated by dividing the weight of cement taken by the volume of liquid displaced, the specific gravity of which latter need not be known. Illustrations of several forms of apparatus will be found in most catalogues of chemical apparatus; some of those most generally used may be briefly described.

Mann's Gravimeter.—This, probably the first piece of apparatus of the kind, was fully described by its inventor in *Proceedings Inst. C.E.*, vol. xlvii., p. 251. It consists of a flask holding, when filled to a mark on the neck, 1,000 grains of water, and a burette with a stopcock con-

taining an equal volume, less the quantity displaced by 1,000 grains of the heaviest substance intended to be examined. 1,000 grains of cement are weighed off and transferred to the clean dry flask, or the flask may be counterpoised and the cement weighed in it. The burette is filled to the containing mark with whatever liquid is used, which is allowed to run into the flask until it is nearly filled to the mark. To expel the occluded air some operators cork and shake the flask, which is a slovenly method. We prefer to hold it by the neck with a test-tube holder, and stir the contents with a stout knitting needle until no more air escapes. The adhering cement is washed off the needle by drawing it up through the liquid, which rapidly rises to the upper part of the flask when the contents are allowed to remain at rest. More liquid is then allowed to run from the burette until the mark is reached. The stem of the burette is so graduated that the specific gravity is at once read off.

Schumann's Volumeter.—This consists of a flask or bottle of about 150 c.c. capacity, into the neck of which is ground a tube graduated upwards from a short distance above the neck from 0 to 40 c.c., divided into tenths. The bottle and part of tube is filled to either the 0 or one of the lower graduations with paraffin or turpentine, and 50 grammes of cement are allowed to fall down the tube into the liquid. The apparatus is carefully shaken to expel the air, and the height of the liquid is read off on the tube. The difference of the readings gives the volume of liquid displaced. The great trouble with this apparatus is caused by the cement, which, from having to follow the liquid down the tube, adheres to its sides. This may, however, be obviated by pouring the liquid down a funnel with a long narrow stem, which ought really to be supplied with the instrument. The cement can conveniently be introduced through an ordinary funnel with a short stem.

Blount's Volumeter.—This is a simple piece of apparatus which is capable of giving good results. It consists of a flask with a broad flat bottom, containing, when filled to a mark at the lower part of a slender neck, which is closed by a stopper, exactly 64 c.c. Above this mark the neck is divided into tenths. The first graduation is marked 14, and not 64; the neck therefore reads upwards from 14 to 17 c.c. To make a determination, 50 c.c. of liquid, either paraffin or turpentine, are delivered into the flask by a pipette; the neck is thus kept dry. 50 grammes of cement are then introduced, and the flask is shaken gently to expel the air. 14 c.c. of the displacement are accounted for by the flask to the first graduation, the remainder is read off on the stem. The volume of liquid displaced by 50 grammes of any sample of Portland cement will fall between 14 and 17 c.c.

Keates' Double Bulb Specific Gravity Bottle.—In this instrument a constant volume of liquid is employed, and a variable weight of

cement. In those previously described the weight of cement has been constant, the volume of liquid varying. It consists of two bulbs placed one above the other, with a short neck between them, the lower bulb somewhat exceeding the upper one in capacity. The upper bulb has a short neck closed by a stopper. On the neck between the bulbs is a mark *b*, on the neck of the upper one is a similar mark *a*. The capacity of the upper bulb must be accurately determined, and may conveniently be 1,000 grains of water at 15.5° C. To make a determination, the lower bulb is filled with a pipette to the mark *b* on the neck with whatever liquid is employed, and the flask is weighed. The cement is dropped carefully into the bottle through a funnel with a short stem until the liquid reaches the mark *a*, when the flask is again weighed. The weight of cement required to raise the liquid from *b* to *a* is its specific gravity.

Fallacy Underlying the Test of Gravity.—It is difficult to understand why this test has become so general, especially in this country. It is commonly supposed that the perfectly burned clinker has a higher specific gravity than that which has been more lightly burned, and that the specific gravity of that less fully burned is higher than that of the yellow slack. Nothing can be farther from the truth. When taken fresh from the kiln, there is practically no difference in the specific gravity of any of the products, provided the carbon dioxide has been entirely expelled. This we have frequently tested in practice, and the following are the results of one set of experiments:—

Four samples were taken from one place in a kiln.

No. 1. A piece of yellow slack burned.

No. 2. A piece of perfect clinker.

No. 3. A piece of lightly-burned clinker, showing in places white spots of lime.

No. 4. A piece of slag-like overburned clinker.

These were ground up and the specific gravity of each was taken in a bottle, the liquid used being paraffin, the specific gravity of which was taken in the same manner.

No. 1. Specific gravity 3.16.

No. 2. „ 3.17.

No. 3. Specific gravity 3.20.

No. 4. „ 3.19.

As carbon dioxide and water are absorbed from the air, the specific gravity gradually diminishes, an aerated cement will, consequently, give lower results than one newly ground from freshly-burned clinker. The specific gravity may, in fact, really be regarded as a measure of the amount of aeration a cement has undergone. A lightly-burned cement, or one containing underburned material, will absorb carbon dioxide and water much more rapidly and to a greater extent than one ground from entirely hard clinker. A low specific gravity may, therefore, for this

reason indicate light burning, or the presence of underburnt material. It must, however, be remembered that the extremely finely-ground cement, so much of which is now coming into the market, is much more absorbent than that more coarsely ground, and it may thus, after the same amount of aeration, give a lower specific gravity. It has been suggested that previous to the determination the sample should be heated at a temperature of 100° to 150° C. This treatment would leave it practically unaffected. The water absorbed exists in combination with lime as calcium hydrate, and it is almost needless to add that neither this nor the carbon dioxide would be driven off at the proposed temperature. Another suggestion is to expel water and carbon dioxide by heating the sample to redness. From what has been said it is obvious that after this treatment the highest possible specific gravity would be the result and the test would be of no value. Most specifications require the specific gravity to be not less than 3·1, which can easily be attained, as we have seen, by very badly-burned cements which have been insufficiently purged.

CHAPTER VIII.

**PREPARATION OF THE MIXTURE OF RAW MATERIALS
BY THE WET METHOD.**

CONTENTS.—Uniform Mixture Essential—Preparation of Slip—Original Process of Portland Cement Making—The Washmill—Modern Washmill—Dimensions of Washmill—Sieves and Screens—Backs—Distribution of Slurry—Subsidence of Solids—Proportioning the Ingredients—Drying Floors—Experiment with Slurry—Goreham's Process—Grinding the Slurry—Margetts' Process—Michele's Washmill—Use of Tubemill for Wet Grinding—Grinding with Abundance of Water—Foreign Methods of Working—Making Slurry into Bricks—Use of Rotary Driers—American Practice—Use of Shaft Kilns.

Uniform Mixture Essential.—It is not only necessary that the correct proportion of carbonate of lime to clay should be maintained, but the mixture must also be uniform and its constituents must be in an extremely fine state of subdivision. This is attained in practice by one of two methods—(1) By the wet process which is applicable only to soft materials, the correct quantities of the ingredients being ground in the presence of more or less water, or (2) by the dry process in which the perfectly dry materials are ground together, although in some cases they are roughly ground separately, the coarse powders being subsequently mixed in the required proportions and afterwards finely ground. Under certain circumstances, even when employing the wet process, the materials may with advantage be ground separately.

Preparation of Slip.—We will now proceed to describe the methods employed for preparing the slip or slurry of the wet process, leaving the treatment of the raw flour or meal, made use of under the dry process, to be dealt with in another chapter.

It is interesting to notice here that Aspdin, the original inventor, insists upon the reduction of the ingredients to a "state approaching impalpability," and this is as true now as it was in his day. Probably more failures with the use of cement have been due to neglect of this precaution than to any other cause, even including the employment of incorrect proportions of the constituents. An imperfect, coarsely-ground mixture, when once it has reached the kilns, is to a great extent past redemption. If it is known to be faulty, it may to some extent be corrected by very hard burning—that is, if the mixture is so proportioned as to admit of this treatment. Some improvement may be effected by watering and storing the clinker before grinding, and by

grinding it to an extreme degree of fineness, but the resulting cement can never possess the properties of that made from carefully-prepared materials, and too often the error is not found out until the product has passed into the warehouse, or worse still into the hands of the consumer.

Original Process of Portland Cement Making.—The plan originally adopted was to incorporate together the chalk and clay—which were the only materials then employed—and at the same time to bring them into a fine state of subdivision in the presence of water in the contrivance known as the washmill. The thin slip or slurry was allowed to flow into large reservoirs or “backs,” from which, as the solid matter settled, the water was from time to time drained off. This method, though now to a great extent discarded in this country, is still in use at some of the older works, and it will be proper to describe it somewhat fully.

It seems highly probable that the cement maker, in the early days of the manufacture, availed himself of many of the processes of the brickmaker, who, long before Portland cement was thought of, had learned to prepare his clay, to add the necessary amount of chalk and to settle the slip in reservoirs much in the same way as is still practised in the South of England, adopting, in fact, processes which date back to the period of the Pharaohs. At any rate, in the London District, which, as already stated, soon became the chief seat of the Portland cement trade, the brickmaker had for generations made use of the washmill and the reservoir or back for the slip, and these contrivances remained until comparatively recent times in common use at cement factories, but little changed or modified. There can be no doubt that for soft materials like the grey chalk and for the alluvial river mud or gault clay the washmill is an excellent contrivance, but when we have to deal with the hard flint bearing upper chalk even the best arranged washmill leaves much to be desired.

The Washmill.—The washmill (Fig. 2) consists in its essential features of a circular or octagonal tank, usually from 14 to 18 feet in diameter and from 4 to 5 feet deep, with a central mound or pier carried above the working level of mill, and of such diameter as to leave round it an annular space or trench 4 to 5 feet wide. The central pier carries the footstep bearing of a vertical shaft, which, by means of gearing arranged on timbers carried by walls at the side of the mill, is driven at a speed of from 12 to 20 revolutions per minute. In the older type of mill this shaft carries a horizontal beam to which are attached strong vertical iron blades, reaching nearly to the bottom of the trench or raceway. An overflow is arranged by lowering a portion of the outside wall, so as to leave a space from 2 to 3 feet long and about 1 foot 3 inches deep. This opening is fitted with a strongly-made wooden frame, covered with brass or copper wire gauze, having about 900 meshes to the square inch. The walls

are sometimes raised above the ground level in order to protect the workmen; a space or spaces being arranged for feeding. The chalk and clay are introduced into the mill, either continuously or from time to time at

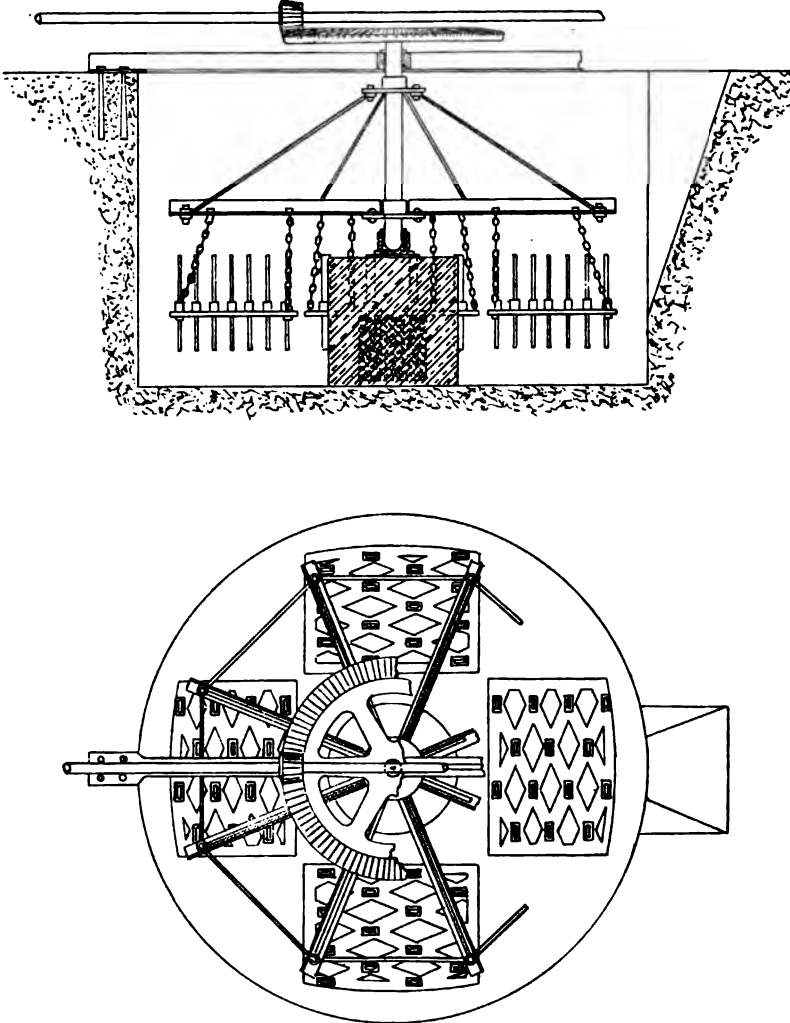


Fig. 2.—Washmill—Section and plan.

stated intervals, together with such a regulated supply of water as to keep the contents constantly at the overflow level. By the action of the knives on the revolving beam the contents of the raceway are violently agitated, the clay is broken up while the lumps of chalk are comminuted by attrition and ground to pieces. These substances are also evenly dis-

tributed throughout the water and are converted into a creamy liquid, termed the "slip," which is driven through the meshes of the sieve by the scour, and is led away by troughs to the depositing backs.

Modern Washmill.—In the modern type of mill, harrows are substituted for the beam with knives. These are formed of cast iron, fitted with steel tines or teeth, and they are suspended by chains from iron radial arms, which are attached and braced to the vertical shaft and to each other. The suspended harrows adapt themselves better to the deposit of stones and flints which collects in the bottom of the raceway than does the rigid beam in the older form of mill.

In some cases harrows have been replaced by heavy edge-runners for dealing with hard chalk free from flints, and mills of this type have given good results. For soft chalk they are unnecessary, as harrows will do the work quite as efficiently, while for chalk with flints edge-runners are obviously unsuitable. Our own experience goes to show that fairly hard chalk, such as occasionally occurs in the South of England, may be very effectually triturated in a mill fitted with harrows if the raw material be broken reasonably small, and if the feed is not excessive. This statement, however, does not apply to the indurated chalk of Yorkshire or that of the North of Ireland.

The brickwork employed in the construction of the mill should be built in cement, and the walling should at least be faced with very hard bricks. The raceway should likewise be paved with hard material, such as granite setts or the burrs of worn-out millstones, and these should also be set in cement.

The question as to whether the materials should be weighed or should be measured into the washmill has often been debated. If the materials were invariably in the dry state, there could be no dispute as to which plan would give the most accurate results, but in their normal condition they contain more or less water, and they are also very absorbent; the quantity of water present consequently varies in accordance with the state of the weather. If equal quantities of each material were used, and if each was equally absorbent, it is evident that weighed quantities might be employed in all conditions of weather; but the quantity of chalk being in round numbers three times that of the mud or clay, any proportions adjusted for use in dry weather would, if used after much rain, result in an overlaid mixture. Since, however, the materials do not alter in volume by absorption of water, measured quantities will practically always contain the same amount of solid matter, and may therefore be used with safety in both wet and dry weather.

Dimensions of Washmills.—In some cases washmills are constructed of much larger dimensions than those we have given, the waggons of chalk and clay being weighed as they are brought alongside, and tipped directly

into the mill. Much better results are, however, obtained from feeding the mill in smaller quantities from wheelbarrows, one barrow-load of clay being tipped in at the same time as its exact equivalent of chalk. A reserve of each material should be kept in hand, and the work may thus go on continuously, the mill never becoming overloaded.

Sieves and Screens.—The sieves or screens through which the slurry leaves the mill should be kept constantly under observation, and should at once be replaced if found to be torn or damaged. The raceway from time to time requires cleaning out, especially when the upper chalk with flints is used. This precaution should not be neglected, for otherwise, as soon as the harrows begin to drag and tilt about on the uneven accumulation which gradually forms in the bottom of the mill, the efficiency of the operation is much impaired.

Backs.—The backs are frequently of large size, being sometimes as much as 100 feet in length by 40 feet in width, with a depth of about 4 feet. A back of these dimensions would thus contain 160,000 gallons of slurry. The sides are generally constructed of dwarf walls of brick or concrete, and the bottom is carefully formed of porous materials, so as to permit of the ready soaking away of the water. It is of course imperative that special attention should be paid to the subsoil drainage.

Distribution of Slurry.—The stream of liquid slurry, on leaving the washmill, flows into a channel, which delivers it to wooden troughing carried round the backs. The wooden troughs are provided at suitable intervals with apertures, from which, by means of slides, the slip may be made to enter any particular back at different places. By changing the place of admission every day, it thus becomes possible to obtain a much more even distribution of the slurry, and this is an important matter, as, from the nature of the means employed to produce it, the slurry, as it leaves the mill, may not be always of normal composition. Thus at some moments the chalk may be in excess, at others the clay, though the average over a considerable period of time is about right. By the occasional use of a drag formed of a piece of plank attached to the centre of a long rope, which is pulled about by two men, the various washings are "luted" or mixed together, and a sufficiently uniform result is obtained. Catch-pits or depressions are provided in the channel leading from the washmill, and into these any unground particles of chalk or coarse sand subside from the slowly-flowing stream of slurry; the coarse sludge deposited in the pits being from time to time removed with a scoop.

Subsidence of Solids.—The suspended chalk and clay, when they come to rest in the back, rapidly subside; part of the water soaks into the ground or evaporates, but a considerable quantity of the clear supernatant liquid is drawn off by means of the "peg-board," which is a

perforated penstock having numerous small openings closed by pegs, the holes being arranged at such levels that the water can be run off gradually as far as the top of the slurry. Some weeks must elapse, even in the summer time, before the contents of the back become sufficiently consolidated to dig them out for removal to the drying floors.

Proportioning the Ingredients.—In the early days of the Portland cement industry, the correct adjustment of the proportion of carbonate of lime to the clay was purely an empirical process, and was in fact an application of the system of trial and error. In the first place, mixtures of the constituents were made in varying proportions, from which samples of cement were prepared, and the samples giving the best cement were adopted. Any irregularities due to variations in the chemical composition of the materials, or to carelessness on the part of the workmen employed at the washmill, were ascertained by occasionally sampling the contents of a back in the course of being filled, and the samples of slurry were then dried and burnt in a trial kiln. From a close observation of the resulting cement, when tested for soundness, colour, &c., the "sampler" was by long experience enabled to judge whether the correct proportions were being maintained. Any error discovered at this time was corrected by altering the proportions at the washmill, agitating the contents of the back, and again sampling. Rapid chemical methods of analysis, to which we have referred, have rendered this system of sampling obsolete, and most cement works now employ at least one competent analyst; but even only twenty years ago, with some very few exceptions, no chemist was employed in any English cement manufactory.

Drying Floors.—When it has become sufficiently dry to admit of this treatment, the slurry is dug in a plastic state from the backs, and is removed to the drying floors, either in deep-sided barrows or in small tipping waggons. The drying floors are heated by passing under them the waste burning gases from coke ovens; these gases are conveyed in flues, which, in the vicinity of the ovens and for about 10 feet beyond them, are covered by fireclay slabs. Beyond this distance the covering is formed preferably of cast-iron plates, diminishing in thickness from about $1\frac{1}{2}$ inches at the commencement, where the iron plates join the fireclay slabs, to about $\frac{3}{4}$ inch at the farther end, where the flues join the main or gathering flue into the chimney. This latter flue is provided with a damper, in order to regulate the draught. The floor is made of sufficient length to utilise all the heat from the ovens, the object in providing the ovens not being to make coke, which can be more cheaply purchased, but to dry the requisite charge of slurry. The front of the floor immediately over the ovens is covered to a greater depth with the slurry than the back, and the thickness of the material is so regulated that the floor may be stripped and re-covered every day. The ovens are

likewise drawn and re-charged every day, and with careful working a weight of coke equal to about half that of the coal employed is obtained. The coke thus produced, supplemented by gas coke, is used in the kilns for burning the slurry into clinker.

Modern Systems of Drying.—This system of drying has given place in recent times to more economical methods, although we believe it is still to some extent employed in the older works. The price of gas coke has risen enormously during the last few years, but its cost has, as a rule, been less than that of coke produced in the somewhat extravagant manner described in connection with the drying floors. The tendency of modern practice has been to utilise the waste gases from the burning kilns in order to dry sufficient slurry for the succeeding charge. Even when this is not possible, as, for instance, in kilns of the continuous type, methods are now available which are much more economical than those above described.

It has frequently been maintained that the slurry passing from the washmill settles irregularly in the backs, the chalk and clay having, it is alleged, a tendency to separate owing to the difference of their specific gravities. If the slurry is finely washed there is no such separation, but if coarsely washed, and if no provision is made for taking out the larger particles of chalk by catch-pits, these coarse particles have a tendency to settle, and may accumulate in the lower layers of the contents of the backs.

Experiment with Slurry.—In order to decide whether separation really took place in the case of carefully-washed slurry, the following experiment was conducted many years ago by one of the authors. A water-tight wooden trunk, 8 feet high and 6 inches square, was prepared, and fixed in a position where it was free from vibration and safe from disturbance. This vessel was filled with slurry collected from one of the shoots entering the backs. When this slip was tested by washing through a sieve having 120 meshes to the lineal inch, it left less than 5 per cent. of very fine grit, calculated on the dry slurry, which contained 75·5 per cent. of carbonate of lime. The supernatant water was drawn off every few days by means of gimlet holes bored in one side of the wooden trunk. When the column of slurry had settled into a stiff mass in which it was evident that no further deposition would occur, the trunk was carefully conveyed into a warm place, and stood in a vertical position until the contents were dry. The wooden sides were then removed and the column of dry material was sawn into a series of short lengths, in each of which the carbonate of lime was accurately determined, with the result that there was practically no difference in the composition of any of the layers from the top to the bottom.

Goreham's Process.—The system of washing the ingredients to a very liquid slip has been practically superseded in this country by the

process of wet grinding with a minimum of water, which was patented by Mr. W. Goreham in 1870, but which has been used in France, at Meudon, in the neighbourhood of Paris, for more than one hundred years, in the preparation of hydraulic lime from a mixture of chalk and clay. The original inventor of this milling process is said by Mr. Henry Reid to have been M. Dupont, and the French works are still being carried on very much on the old lines.

Under the Goreham system, the fine sieves on the washmill are replaced by grids, the bars of which are fixed $\frac{3}{8}$ inch apart, or, in some cases, perforated plates are employed. The chalk and clay are fed into the washmill exactly as in the case of the older method, but only sufficient water is used to produce a thick slurry, which, in the best practice, contains not more than from 40 to 50 per cent. of water.

Grinding the Slurry.—From the washmill the coarse, roughly-mingled slurry is lifted by a scoop wheel or bucket-elevator to a shoot leading to the grinding mills, from which it is tapped, the flow being regulated by slides. The mills employed are of the ordinary flour-mill type, formerly so generally used for grinding cement, fitted with French burr stones, as for dry grinding. Originally the slurry flowed from these mills directly to the drying flats, but with the introduction of chamber kilns, which required its delivery at a higher level, the practice became general of collecting the slurry in a tank or well, from which, by means of specially designed and powerful pumps, it is lifted and delivered through pipes to any required point.

Economy of the Process.—This process leads to a great economy of time and involves much saving of space, as the backs are entirely dispensed with, while the cost of grinding and pumping the slurry is much less than that of emptying the backs. The saving of cost was, however, not great, so long as the drying was effected on flats heated by coke ovens, since more water had to be evaporated from the pumped slurry than in the case of that taken from backs, especially when it was possible to allow the slurry to remain a sufficient time in the backs to become thoroughly stiff.

Margetts' Process.—The above described method of preparing slurry has now become almost universal in English practice. We may, however, refer to two processes by which thick slurry is produced without wet grinding. The first of these entails the use of the sieve devised by Mr. W. G. Margetts, which is especially suitable when soft, easily-triturated chalk free from flints is employed. The slurry is mixed in the washmill with the minimum of water, the overflow being arranged to take place through perforated plates having holes through them about $\frac{3}{8}$ inch in diameter. The feed of the ground mixture is in a continuous stream, and it enters the bottom of a sieve, shaped like an inverted pyramid,

revolving at a speed of about 150 revolutions per minute; the sieve employed has from 20 to 30 meshes per lineal inch. During its passage up the sides the finer portions of the material pass through the meshes,

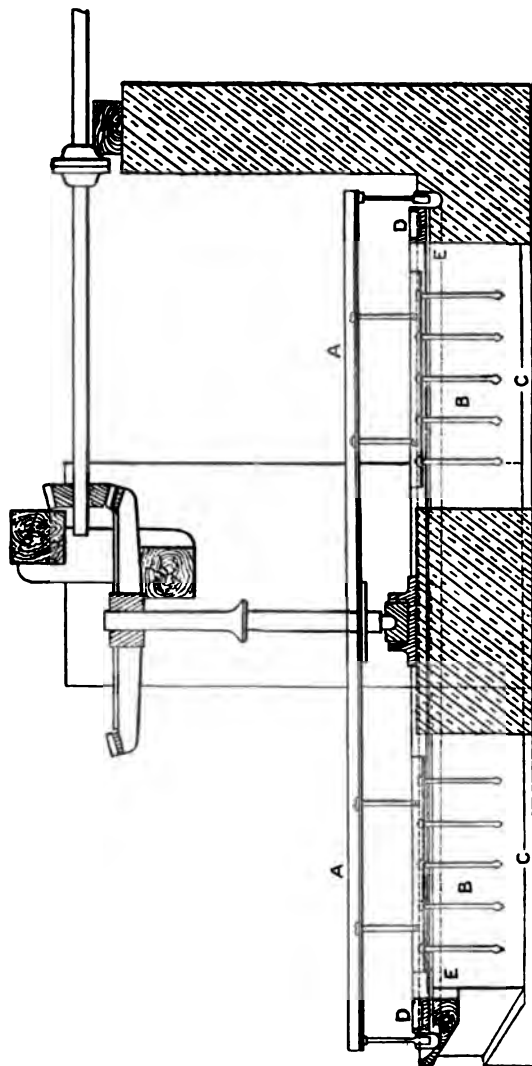


Fig. 3.—Michele washmill.

and flow away to the pumps; the coarse particles, on reaching the top, are ejected into an outer casing, and are thence returned to the washmill. For chalk with flints the method is obviously unsuitable, as even small fragments of flint would rapidly destroy the sieves. With respect to the

efficiency of this process, it may be mentioned that the manufactory in which it is employed was one of the first in this country to guarantee its cement to stand accelerated tests, which can only be obtained with certainty when a very carefully-prepared mixture of raw materials is available. Mr. Margetts, in a letter to *The Engineer*, on 22nd May, 1891, stated that his practice was to submit the briquettes to the action of boiling water instead of to a temperature of 180° , as is usually prescribed.

Michele Washmill.—M. V. D. de Michele patented, in 1877, an improvement in the washmill which enabled further grinding to be dispensed with. The minimum quantity of water is still employed, but the slurry, instead of flowing out at one spot in the circumference of the mill, overflows through metallic surfaces which entirely surround the outer wall. The lower surface plate, forming the rim of the mill, is fixed; the upper one revolves with the stirring apparatus of the mill. A section of the mill is shown in Fig. 3. It will be understood that the grinding surfaces are provided with a certain amount of lead or swallow. To enter the grinding rings at all, the materials must previously have undergone a considerable reduction in the mill, and, before reaching the flat or grinding surfaces, coarse particles which may have entered are further reduced in size in the gradually contracting swallow.

Use of Tube-mill for Wet Grinding.—With flint chalk all the wet grinding processes require great care and attention. Small pieces of flint pass through the washmill grids and have a tendency to lift the stones, thus allowing the slurry to pass through without undergoing reduction. The time is probably not far distant when the tube-mill, to be described when dealing with systems of dry grinding, will altogether displace mill-stones for grinding slurry, especially in new plants. It is already used for this purpose in several American and Continental works, employing the wet process.

Process is necessarily Continuous.—It will have been observed that the wet milling process, as previously described, is a continuous one, the stream of slurry flowing, without rest, from the washmills to the grinding mills and from thence to the pumps. Some little bulking may take place in the small tank, sometimes placed to feed the mills, and in the pump-well, which would probably receive the slurry from several mills. No attempt, however, was originally made to mix the slurry, either before or after the wet milling, as it was assumed that the stream flowing from the washmill was fairly constant in composition. This, however, is not the case even when using materials which vary little from day to day, such as are generally available in England for cement making. Even when the utmost care is taken in feeding the washmill, the relative proportions of carbonate of lime to clay constantly fluctuate. The old method of sampling ceased to be of any value with the disuse of backs,

as, before the result obtained in the case of any given sample could be known, the material sampled would have passed beyond hope of alteration. In fact, at the present time, when rapid methods of determining carbonate of lime are employed, it is not an easy matter to keep the average composition even fairly constant.

Advantage of Grinding with more Water.—It is difficult to understand why, for the sole purpose of obtaining slurry with from 40 to 50 per cent. of water, wet milling and the disuse of backs have become so general in this country. The slurry is certainly no better and is often much worse than that prepared by the older method. A course, combining the advantages of both methods, would be to wash together the ingredients in the original manner, with from 70 to 80 per cent. of water, to collect the slurry in smaller and deeper backs and to draw the water from the surface until the contents were sufficiently stiff. From 30 to 40 per cent. of water can rapidly be got rid of in this manner, the area required for backs would be comparatively small, and by constructing the backs with sloping bottoms, and providing a system of suction pipes with stop-valves, the pumping could be easily managed, while there would be the additional advantage of always holding a stock of slurry, the composition of which is known to be accurate.

Methods of Regulating the Composition of Slurry.—During recent years not only has greater attention been paid to the fine grinding of slurry, but means have also been devised for ensuring its more accurate and uniform composition. Generally the method for effecting this is as follows:—The slurry from the grinding mills is collected in one of two large circular tanks fitted with revolving arms for agitating the contents. When nearly full the stream of slurry is diverted from the first tank to the second, and a sample is taken from the first tank. This is tested for carbonate of lime, and if the proportions are found to be correct the contents of the tank are allowed to pass onward. Two smaller tanks are likewise provided, one containing slurry prepared from chalk only, the other consisting of finely-washed clay. If the proportions in the large tanks are incorrect, the required addition is made from one or the other of these smaller tanks, and the mixture is again sampled and tested. This operation may be repeated if found to be necessary, and the contents of the tank are not finally discharged until they are proved to be of normal composition.

Mode of Working adopted Abroad.—On the Continent, the wet process, when it is employed, generally follows very closely the original English practice, so far as the preparation of the slurry is concerned. This involves the use of the washmill, the slurry being allowed to settle in backs. Wet grinding is not general, but when it is practised more water is employed than is usual in England. The use of "dosage" tanks

for adjustment of proportions is general, but in some cases, when the materials are of very uniform composition, the slurry flows direct from the washmill to the backs. When this adjusting process is employed the plant consists of washmill "dosage" tanks, and two smaller washmills, in which the dosage of chalk or marl, and of clay is actually prepared.

Slurry Moulded into Bricks on the Continent.—It has been mentioned that the almost universal practice at the present time in this country is to dry the slurry by the waste gases from the kilns. The methods for doing this will be described when dealing with kilns. On the Continent this system is not usual, the process of drying is generally conducted independently. The method employed is to allow the slurry to remain in the backs until it becomes sufficiently stiff to be pugged and made into bricks; it is used much stiffer in fact than was the practice in England when drying was carried out on flats. This entails the provision of a much larger system of backs than would be otherwise needed. The bricks are now almost always dried in tunnel driers, which consist of a series of tunnels from 100 to 120 feet in length, through each of which a large volume of air is driven, heated by passing it through a furnace. The bricks, as taken from the machine, are stacked upon waggons which pass continuously through the tunnels in the opposite direction to the current of heated air. They are thus first exposed to the action of the air which is leaving the tunnel, and which has lost much of its heat and has become charged with moisture. As the waggons gradually pass onwards they encounter drier and hotter air, until on reaching the further end they have become perfectly dry and ready for the kiln. The bricks may remain in the tunnel, which is kept constantly filled with waggons, for about twenty-four hours. One tunnel, 100 feet long with two waggon-ways, will dry from 7,000 to 8,000 bricks in the twenty-four hours; the efficiency being stated to be an evaporation of about 13 lbs. of water to the pound of fuel.

Employment of Rotary Driers.—The time during which the slurry remains in the backs is frequently shortened by drying a part of it in rotary driers and mixing this in pugmills with wet slurry in such proportions as to bring the whole mass into a fit consistency for being made into bricks. The rotary drier is a slightly-inclined, slowly-rotating cylinder, from 30 to 40 feet in length and from 4 to 5 feet in diameter. The products of combustion and the heated air from a furnace constructed at the lower or discharge-end pass through the cylinder in direct contact with the material to be dried, which is continuously fed in at the upper end. Various devices adapted to the material under treatment are employed to bring it into contact with the hot gases during its passage through the cylinder, to facilitate its progress, and to prevent

it from adhering to the interior lining. In some forms of the apparatus, the hot gases first circulate round the outside of the cylinder and then pass through the interior in the opposite direction to that in which the material is travelling. A rotary drier working on slurry will evaporate approximately 10 lbs. of water per lb. of fuel.

Brick-making at English Cement Works.—The system of making the slurry into bricks has been to some small extent adopted in England, but the cost of labour will probably prevent its very general application in this country. At the same time it must be remembered that, with the use of dry slurry, kilns may be employed which are much more economical in fuel consumption than those which are now used both to burn the material and also to dry a sufficient amount of raw slurry for the succeeding charge.

American Practice.—In America, soft and sometimes wet marls from the beds of wholly or partially dried-up lakes are largely used. The deposits in question vary in depth and are sometimes overlaid by peat or soil, while beneath them are frequently found beds of good cement clay. The methods employed for obtaining the marl are adapted to suit its condition in the bed. In dry situations, mechanical excavators are used both for removing the surface soil or peat and for extracting the marl, which is deposited in waggons for removal to the works. If the deposit occurs at the bottom of an existing lake, it is obtained by means of dredging and the loaded barge is then brought as near as possible to the works in order that the contents may be discharged by pumps into receiving tanks. The same method is employed in swampy ground, in which case a grab-dredger is used. Under these circumstances the excavated portion becomes filled with water, and the dredger thus forms its own channel as it moves forward.

When extracted in this way, the marl is frequently too stiff to pump and yet too soft to be easily placed in waggons. If waggons are used, the grabs discharge into them direct, and the waggon-roads are in this case laid alongside the channels. It is sometimes possible to arrange that the transport to the works shall be effected by conveyor-belts. If pumping is resorted to, the grabs deliver their contents into a pugmill fixed on the barge and sufficient water is added to produce a thick slurry which is allowed to collect in the bottom of the barge. This liquid slurry is either pumped through a pipe-line, arranged on trestles, passing from the barge to the receiving tank in the works, the pipes being shifted as the excavation proceeds, or a pipe is laid from a fixed point to which the barge is brought, as in the case of dredging from a lake.

Modes of Dealing with Different Materials.—The treatment of the materials varies considerably, scarcely any two works adopting the same

methods, but, whatever may be the mechanical means employed, great care is invariably taken to ensure the accuracy, fineness, and uniformity of the mixture. The washmill is not in favour in America, but tanks fitted with arms attached to a revolving vertical shaft are in frequent use for stirring. In some cases the stirring is done by means of blowing in compressed air, for which purpose a number of small pipes from the mains are conducted so as to reach nearly to the bottom of the mixing tanks. The mixture of the marl with clay is generally effected by heavy edge-runners, working in large pans; wet milling is carried out either by the use of the tube-mill, or by means of mills consisting of vertical steel discs revolving at a high speed in opposite directions. The slurry is introduced at the centre of the discs through a hollow shaft and it escapes at the circumference into a tank placed beneath. When rotary kilns are employed, the wet slurry, which often contains as much as 60 per cent. of water, is pumped direct to the tanks supplying the kilns.

Use of Shaft Kilns.—The use of rotary kilns although general in America is not universal, some of the older works employ a brickmaking process with shaft kilns. Under these conditions, when using hard marls requiring the addition of water, the process follows fairly closely the Continental practice, except that backs are not employed. The quantity of water is restricted as much as possible; a part of the slurry is passed through rotary driers and is used to stiffen a further portion of wet slurry, and the plastic mass is subsequently moulded into bricks which are dried as we have seen in tunnel driers.

With soft, wet marls the same method may be employed with advantage. These marls, however, often occur in such a finely-divided state as to render milling unnecessary, all that is needed is to intimately mix them with the finely-divided clay. This is frequently effected by grinding the clay to powder, after drying it in rotary driers and mixing it in the required proportion with the wet marl, but this does not always produce a sufficiently stiff mixture for brickmaking purposes, and a portion has to be dried in order to temper the remainder to the proper consistency.

CHAPTER IX.

**THE DRY PROCESS: TREATMENT OF THE RAW MATERIALS
BY DRY METHODS.**

CONTENTS.—The Dry Process in England—Use of Lias Materials—Widely different Character of Raw Materials—Drying the Raw Materials—The Preparation of the Raw Flour from Limestone and Clay—Silos—Automatic Weighing—American Practice with Hard Limestone—The Edison Process—The Treatment of Soft Materials—Process Employed in Denmark—German Process—Modified English Process—Preparation of Raw Flour for the Kilns—Brick-making.

The Dry Process in England.—This process had its origin in this country, and was first employed for dealing with the limestones and shales of the lias formation. It has, however, made much greater progress in other countries than it has in our own, for reasons that are easily explained. The materials in the London district, from which the principal shipping trade is done, are much better adapted for treatment by wet than by dry methods. At many places inland, where suitable hard materials for cement making occur, works employing the dry process have sprung up and flourished. These works supply a home market, capable of being reached within a reasonable district by rail; but such factories are entirely shut out of the shipping trade, for cement will not in this country bear previous carriage to a port for shipment, while even when seeking markets in or near a port, manufacturers have to compete with cement brought in by vessels, often at a less cost for freight than the expense of sending by rail to the coast from their own works. The dry process has therefore had, and must continue to have, a limited application in this country; hence it has not progressed so rapidly as in many places abroad, where the nature of the materials render its adoption necessary. Carboniferous limestone is to some extent employed for cement making, but the materials most generally used in England for the dry process are obtained from the lias formation. The nature of these materials, and the system of manufacture adopted for dealing with them, may be briefly considered, before passing on to a general review of the subject.

The Use of Lias Materials.—The lias formation consists of layers of impure limestone of varying thickness, parted by seams of shale or clay—the total thickness of the latter beds generally considerably exceeds that of the stone. As regards contents of carbonate of lime, the layers of

stone vary considerably; in some cases they approach very closely to that required for a cement mixture. Complete analyses of typical lias limestones have been given on p. 11, and in the following table are the results of partial analyses of 24 layers or "floors" of stone from a quarry in the Midland counties, the partings consisting of clay. In any one selected lias quarry, the percentage composition of the clay in the layers of stone may be taken as being representative of all the others. This is not true of the shales and clays which are very irregular in their composition. Some are high in magnesia, while others often contain sulphur combined with iron as iron pyrites to such an extent as to unfit them for cement making. Analysis No. 1 is that of the top layer.

No.	Silica.	Oxide of Iron.	Alumina.	Carbonate of Lime.	Carbonate of Mag.
1.	13.30	2.89	4.08	77.52	1.23
2.	14.20	3.08	4.36	74.71	1.13
3.	12.14	2.64	3.73	78.41	.98
4.	11.63	2.53	3.57	79.45	1.24
5.	11.04	2.40	3.40	79.92	1.46
6.	11.17	2.43	3.43	79.39	1.40
7.	13.11	2.85	4.13	76.29	1.36
8.	10.13	2.20	3.11	81.69	1.40
9.	10.15	2.27	3.12	81.05	1.54
10.	10.78	2.34	3.31	80.49	1.24
11.	14.06	3.05	4.32	74.81	1.25
12.	11.03	2.40	3.41	80.22	.91
13.	10.16	2.22	3.13	81.82	1.40
14.	12.44	2.70	3.83	77.14	1.05
15.	11.71	2.54	3.58	78.47	2.22
16.	13.31	2.90	4.09	76.37	1.72
17.	12.81	2.78	3.91	75.53	2.91
18.	11.73	2.56	3.60	78.49	1.34
19.	9.75	2.13	3.00	80.87	2.31
20.	10.30	2.24	3.17	80.30	1.86
21.	10.64	2.31	3.28	78.97	2.01
22.	10.74	2.33	3.32	79.39	2.05
23.	10.08	2.18	3.13	81.21	1.42
24.	15.98	3.47	5.11	70.53	1.17

With such materials as these, the preparation of a mixture of uniform composition is not a difficult matter. It will be observed that the percentage of carbonate of lime in all of them varies but little from that required for a normal cement mixture, and all that is necessary, therefore, is to grind them together with sufficient clay to bring the percentage of carbonate of lime to about 76 per cent. Owing to the close approximation of these limestones to cement mixtures, and the extremely intimate natural admixture of the carbonate of lime and clay, which is far more perfect than anything which can be produced artificially, cement made from them may safely contain 1 or even 2 per cent. more lime than

if made from an artificial mixture of carbonate of lime and clay. The preparation of a uniform mixture is not always so easy a matter as in this case. The following table gives the percentage of carbonate of lime in the successive layers of another quarry, also in the Midland counties. It will be noticed that in this case the proportion of carbonate of lime in the stones is higher than it was in the previous example. The partings between the floors are entirely composed of shale of varying degrees of hardness; those containing the highest percentage of carbonate of lime being invariably the hardest. The line of separation between stone and shale is not, however, very sharply defined. Adhering to the stone, but separating easily from the shale, is a layer of somewhat intermediate material of very irregular composition, from 1 to 2 inches in thickness; this is locally known by the workmen as "scull."

Floor.		Percentage of CaCO_3 .	Floor.		Percentage of CaCO_3 .
No. 1,	Stone,	75.20	No. 5,	Shale,	51.71
" 2,	Stone,	83.12	" 6,	Stone,	88.22
" 2,	Shale,	56.87	" 6,	Scull,	68.54
" 3,	Stone,	85.00	" 6,	Shale,	49.02
" 3,	Scull,	78.39	" 7,	Stone,	84.49
" 3,	Shale,	39.56	" 7,	Scull,	69.59
" 4,	Stone,	86.15	" 7,	Shale,	51.24
" 4,	Shale,	48.59	" 8,	Stone,	81.83
" 4,	Shale,	50.60	" 8,	Scull,	77.13
" 5,	Stone,	88.14	" 8,	Shale,	48.42
" 5,	Scull,	69.65	" 8,	Shale,	58.12

The system of manufacture generally adopted is briefly as follows:—The floors of stone are stripped off one by one; they are cleaned of shale and clay, and when brought to the works are stored under sheds, each layer separately; and the shale or clay is then dried on heated floors. The weighed quantities of each are crushed by a stonebreaker and ground to raw flour, frequently by millstones, which are well adapted for these materials. The treatment of the raw flour varies considerably in different works. In some cases it is pugged with water to a stiff slurry, which is dried either over flues on hot floors, or in chambers heated by the waste gases from the kilns. In others it is made into a wire cut or plastic brick, while in the most modern practice it is pressed into semi-dry bricks, containing about 9 per cent. of water. The method of burning and grinding the resulting clinker will be dealt with when we are considering the whole subject of cement burning. Some of the English works have been equipped with quite modern appliances; the crushed materials are dried in rotary driers, and the product is ground by ball- and tube-mills.

Widely Different Character of Raw Materials.—The treatment of hard materials as regards the first stage, the preparation of the raw flour,

which corresponds to the slurry of the wet process, will now be considered. When the widely different physical and chemical properties of the materials from which Portland cement is now made by the dry process are considered, it will be evident that no method is universally applicable. As examples of the different substances available, we may take the indurated chalk of Yorkshire and the North of Ireland, nearly a pure carbonate of lime, soft as compared with limestone, but more suitable for treatment by the dry process than the wet; the hard crystalline and nearly pure limestone of the carboniferous and silurian formations; the impure limestones of these formations in which the carbonate of lime often falls below that required for a cement mixture and the impure lias limestones previously referred to. Among clay materials may be mentioned carboniferous and silurian shales, carboniferous limestone shales, lias shales and clays, and boulder and alluvial clays.

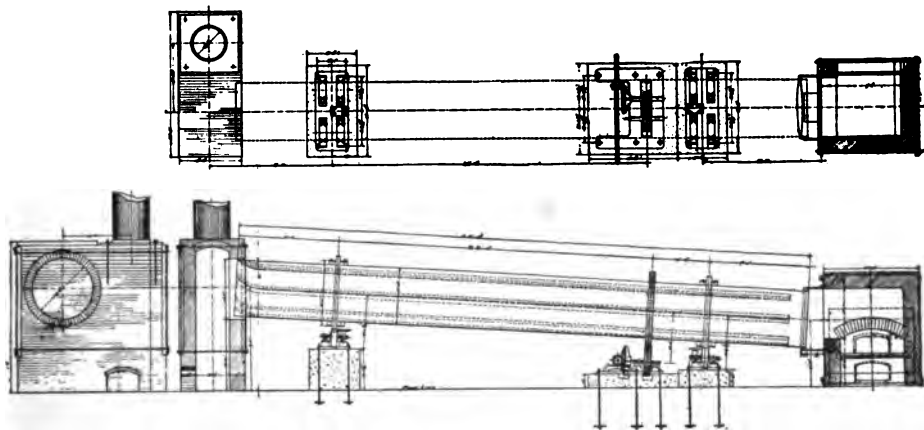


Fig. 4.—Plan and Section of Lathbury & Spackman's Rotary Drier.

Drying the Raw Materials.—Before beginning the grinding, whatever the raw materials may be, they should be absolutely dry. Whenever this is possible the drying should be effected after crushing; the crushed material passing from the crusher through a rotary drier on its way to the grinding mills. This form of drier was described generally at p. 103, when dealing with the question of drying slurry. For the materials now being considered, the apparatus differs in the construction of the interior of the cylinder, which is provided with longitudinal shelves which lift and drop the material as it passes onwards, thus exposing it to the action of the hot gases. The general arrangement of the drying plant adopted by Messrs. Lathbury & Spackman is illustrated in plan and section at Fig. 4, and the drying cylinder, in course of erection, is shown

in Fig. 5. The internal shelves are seen in the section (Fig. 4), which also indicates the inclined position of the cylinders and the position of the furnace. This method is particularly applicable for materials that contain little moisture and which admit of being crushed as brought from the quarries, such as limestone and some kinds of shale. The mixture may, if desired, be made in such cases as these at the time of crushing. With clay or soft damp shale this is not possible, such materials must in the first place be dried before they can be mixed with the limestone. This may be done on heated floors, but it is a somewhat costly process, and, except in small plants or when the addition of only a little clay is necessary, this system is not often employed. Rotary driers may be used, but in many cases the drying kiln or tower is employed.

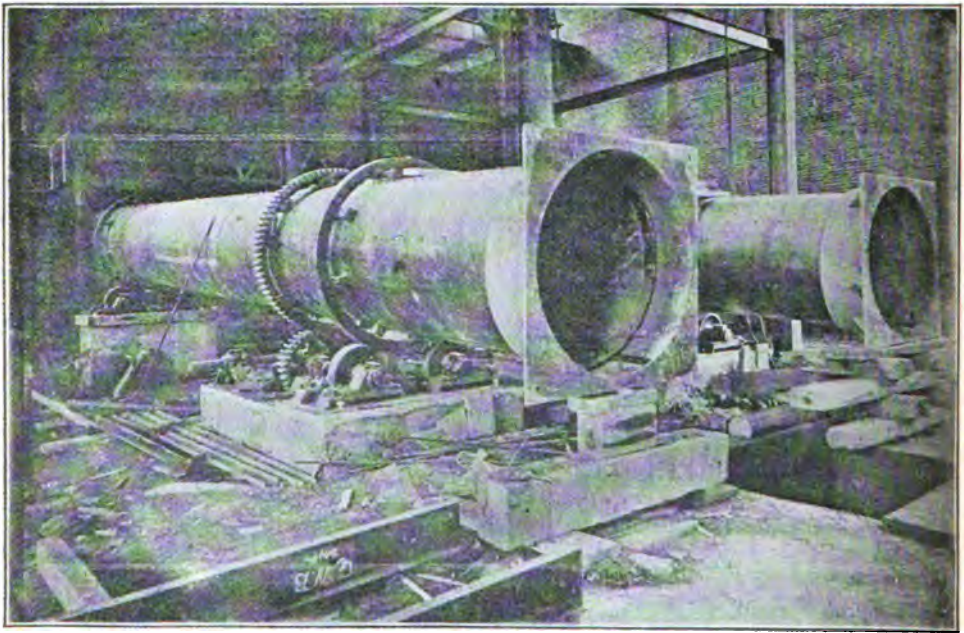


Fig. 5.—Lathbury and Spackman's Driers during Erection.

Employment of the Drying Tower.—This is a vertical tower, often of considerable height, in the lower part of which is constructed a perforated dome of brickwork. Hot air and gases from a furnace enter this dome and pass upward through the perforations, the draught being maintained by a fan at the top of the tower. The tower is kept full of material which is fed in at the top and passes downwards by gravitation, meeting the hotter and drier air and gases as it descends. The contents

are taken out quite dry from a series of openings arranged round the outer wall of the tower. Fig. 6 shows the Smidth tower from a photograph. The square shaft seen on the left contains a lift, by which the material is raised to the top of the tower in small waggons. In some cases a cableway delivers it at the top, direct from the quarry or excavation. So long as the hot air can be uniformly drawn through it, the



Fig. 6.—The Smidth Drying Tower.

tower will work with a moderate proportion of small material, but if the raw material consists principally of small fragment particles it is best to use the rotary drier. Very wet clay should be stored under cover until it has parted with some of its water, otherwise it will be liable to consolidate when tipped into the tower, and it may thus prevent the passage of the heated air. Artificial drying may sometimes be avoided; thus at

the works of the Californian Portland Cement Company, calcite and clay are the raw materials employed; the clay pits are about 30 miles from the works and the clay is ploughed up in patches during the summer, and, after exposure to the hot dry atmosphere until dry, it is brought to the works by rail and stored in bins of 5,000 cubic yards capacity.

The Preparation of the Raw Flour from Limestone and Clay.—Two methods will be described. Both are in actual use, and may be taken as typical of the best modern practice for dealing with limestone and clay. In the first case, the materials are of regular composition and are fairly pure. The clay is dried in towers; the limestone, which is hard and non-absorbent, is not dried, and both these substances are then crushed together in quantities which are weighed by hand; each mixing, which is turned over with the shovel as fed to the crusher, amounts to about 4 cwts. The grinding is effected by Griffin mills, and the material passes direct from the crushers to the supply-hoppers. These are not large, being only of sufficient capacity to ensure a constant supply to the mills. Any attempt to bulk the crushed material at this stage would result in a product of very irregular composition, as the clay and the fine portion of the stone would have a tendency to filter through and separate from the coarser stone, thus giving alternately an overlaid and an overlimed product. The flour from the mills is collected by screw-conveyors which deliver it into storage bins or silos.

In the second case, the limestone is of constant composition, while the clay contains a small but varying quantity of carbonate of lime. Both of these materials are dried separately, and the stone is roughly crushed and passed from the crushers automatically through rotary driers. It is then raised to the feed hoppers of ball-mills, and is reduced to a coarse powder which is elevated and delivered into storage bins. The clay is also dried by rotary driers, and is then crushed between rollers to a powder which is elevated to storage bins, from which samples are withdrawn for testing; the proper proportion of clay to limestone being calculated from the result of each crushing. The coarse powders are both withdrawn from the bins by worms, and the weighing is done by automatic machines, which discharge into a conveyor that mixes and carries the material to tube-mills. In these mills the final grinding and mixing is effected, and from them the flour is taken by conveyors and is elevated to the hoppers supplying the rotary kilns.

Silos.—The employment of silos for containing raw flour has been referred to, and their use may now be briefly considered. Their construction must depend entirely on the purpose for which they are required. With raw materials of uniform composition, and in which little variation in the product is likely to occur, they may be used for storing a supply of flour, and at the same time may serve to equalise

any slight irregularities occurring during the process of crushing and grinding. In this case they are generally of large size, the flour being drawn from them in several places by worms, which all discharge into one mixing conveyor. With irregular materials it is usual to construct several silos of moderate size, the contents of which may be tested before they are drawn out. By simple arrangements of extracting-worms and elevators, these silos may be made to answer all the purposes of the dosage basins of the wet process. It is thus possible to carry out the mixing most efficiently by continuously extracting the flour at the bottom, and elevating and discharging it again at the top, either while the silo is being filled or afterwards. The contents of one silo, if it be overlimed, may be mixed with the contents of another that is overlaid, by withdrawing the contents together and discharging them either into a third silo or into the main conveyor. Again, the contents of one silo, if of incorrect proportions, may be drawn out and discharged into another that is being filled from the mills, the material from which is adjusted to correct that from the silo, while at the same time the mixture may be perfected by continually withdrawing the contents at the bottom, and discharging them at the top during the time that the filling is in progress.

Automatic Weighing.—Reference may be made to a system of automatic weighing, which we believe was devised by the late F. J. Smidth, which enables a very accurate mixture to be made when dealing with two materials when the final grinding is by tube-mills. The materials are ground in a dry condition to coarse powders, which are collected in separate bins. Two "chronos" automatic machines, one for each material, are coupled together in such a manner that the hoppers in which the materials are weighed will only discharge simultaneously, and then only when each of them has received the exact weight of material to which it is set. The coarse powders are withdrawn from the storage bins by worms, and the machines are under the control of the chemist in charge, who regulates them, and who alone has access to them. A counter attached to each machine shows the quantity of material that has passed through. The weighing machines discharge into a screw conveyor, which mixes, and at the same time conducts, the coarse powder to the tube-mills, which both grind and effect a very intimate mixture of the ingredients.

American Practice with Hard Limestone.—The manufacture of Portland cement by the dry process from hard materials has attained its greatest development in America; by far the largest quantity of cement made in that country being produced from limestone. The principal seat of the industry is in the Lehigh Valley, Pennsylvania, the limestone which is employed occurring on each side of the Lehigh River, in the

neighbourhood of Coplay, and also across the Delaware, near Phillipsburg, New Jersey. This stone forms part of the silurian formation, and in some cases is a nearly pure carbonate of lime, in others it consists of hydraulic limestone known as "cement rock," containing from about 68 to 72 per cent. of carbonate of lime. This rock is sometimes of uniform composition, but frequently the percentage of carbonate of lime varies in the different beds. A cement mixture is made of the two rocks, and while the method of preparing and grinding differs in details and in the plant employed, the general principle is the same in all the manufactories. Drying previous to grinding is universal, this being effected by rotary driers after crushing. When each kind of rock is of uniform composition, the quantities are generally weighed at the commencement, previous to crushing. If the composition is irregular, they are roughly crushed, dried, and either very finely crushed or coarsely ground separately, the products being stored in bins for sampling and testing for carbonate of lime. The weighing is carried out by automatic machines. The use of either ball- or tube-mills or of Griffin mills for grinding is almost universal in the most recent plants; in some of the older ones millstones, built either of French burr or of rock emery, are still in use. Silos, as such, are not a feature of American practice, the ground material being generally conveyed from the mills to the hoppers or stock bins supplying the rotary kilns.

The Edison Process.—This is an entire departure from existing methods. The plant is situated at Stewartsville, near Phillipsburg, New Jersey, and is designed to produce 1,500 tons of cement per day, a commencement being made with half this quantity. The materials are cement rock and nearly pure limestone, and the crushing and grinding are effected entirely by rolls. Each rock is coarsely crushed separately. The first rolls are 5 feet wide and 5 feet in diameter. After passing these rolls, the material falls successively through three other pairs of rolls, each of 3 feet in diameter, which reduce it to a size of $1\frac{1}{2}$ inch and smaller. The crushed material is carried by conveyor belts to the driers. These are vertical towers heated by coal fires at the bottom, and filled with inclined cast-iron baffle-plates or shelves, down which the material passes. From these towers it is conveyed by belts to storage bins, the cement rock and limestone being still separate. From these bins each material is weighed automatically, and the mixture is carried by conveyor belts to the fine grinding rolls. The process now becomes a system of grinding and separation. After leaving the rolls, a certain quantity of the material passes in a thin stream in front of the outlet from a blower. Of these there are 16, each of which is provided with a box having muslin sides. The fine dust is blown into the muslin-lined boxes, which retain it, the air passing through the muslin. The coarse stuff falls upon a belt,

and is conveyed back to the rolls for further grinding. The dust, 96 per cent. of which is said to pass a sieve having 40,000 meshes per square inch, is conveyed from the boxes to a floor, on which it falls layer above layer, and is turned over and mixed by a rotating screw. From this floor it is conveyed to the rotary kilns.

The clinker is ground and separated exactly as is the raw material, except that the first, or 5 feet rolls, are here dispensed with. As regards the quality of the product, this process will certainly give no better results than such as are obtained by the methods usually employed in the same district, and which we have previously described. Time only can settle the question of comparative cost. This process certainly violates the generally accepted principle that the constituents should be brought into a state of extremely intimate and uniform mixture, for the system of separating and regrinding is not favourable to the attainment of this result. At the same time it must be remembered that the cement rock, which approaches very closely the composition of a cement mixture, forms from 80 to 90 per cent. of the whole, and the resulting product must consequently be more perfectly compounded than if pure limestone constituted the greater part. One of the most disastrous failures we ever knew resulted from the use of air separators upon a mixture of nearly pure limestone and soft shale.

The Treatment of Soft Materials.—Many works using soft materials manufacture by the dry process ; but, apart from other considerations, the choice of methods must be influenced by the facility with which such materials may be dried. Thus the water in chalk, chalk marl, and many kinds of clay may be easily got rid of, while the sticky, tenacious, alluvial mud used on the Thames and Medway, and the soft American marls, obtained by dredging, could only be dried at a prohibitive cost. If the burning is conducted by rotary kilns, the wet process should certainly be employed, as, although wet slurry requires more fuel to burn it, and longer kilns are needed than for the powder of the dry process, the fuel is better employed in the kilns than in drying the materials before grinding, while the cost of manipulation is less. In the early days of the rotary kiln process in America, it was customary to treat dredged marls by the dry process, a practice afterwards abandoned in favour of the wet treatment. The dry process is again being reverted to in one or two instances, but we question if the results will be commercially successful. Another point which should be taken into consideration is that of climate. In countries subject to severe winters, a wet process plant must necessarily suspend operations during frost, while, by the use of the dry process, work may be continued throughout the year. In the Cambridge district some of the manufactories employ the wet process, others use the dry process, the materials being in all cases exactly similar—viz., chalk

and chalk marl. Many works on the Continent of Europe also employ the dry process for soft materials.

Process Employed in Denmark.—The system adopted at the Aalborg works in Denmark may be here described as typical of this practice. The materials are chalk and clay, which are dried in towers. Each ingredient is crushed separately to a granular condition by rolls, and the required quantities are then weighed by coupled automatic machines. The mixture is carried and further mixed by a screw-conveyor to the grinding mills. These are under-runner mills, fitted with French burrstones 4 feet in diameter. The flour is collected in silos of large size, from which it is withdrawn in several places by worms.

German Process Described.—At a German works using chalk marls an entirely different method is employed. The marls as quarried are weighed in the correct proportions and introduced into an edge-runner mill with a perforated pan. From this mill the mixture passes successively through a rotary drier, rolls to break up any hard nibs, and a tube-mill. This arrangement of pan-mill, drier, rolls, and tube-mill, forms one unit of plant. The fine flour from the tube-mills is moistened with a little water in a mixer of the pug-mill type, and is made into semi-dry bricks. The materials now being considered are very hygroscopic, and if the tube-mill is employed for grinding this must immediately follow the drying, which must be perfect. The tube-mill, except when employed in the wet way, will not work on materials even slightly damp; and unless perfect dryness can be ensured, it is better to employ some other system of grinding. French burr mills will grind materials not perfectly dry, and indeed are very suitable for those under consideration, but a much better output is obtained from a perfectly dry material.

At another German works employing hard and soft chalk marls the system in use is a combination of both the wet and dry process. The hard marls are prepared in the dry way, the soft marls by the wet; the flour in the one case and the slurry in the other being of strictly normal composition. The two are mixed in pug-mills to such a consistency as to admit of being made into wire-cut bricks, which are dried in tunnels. It is evident that in preparing the mixture no care need be taken except to ensure the proper consistency, both materials being normal.

Modified Process Employed in England.—A somewhat similar process has been employed for many years at a small works in England, the materials being a hard crystalline limestone and a soft alluvial clay, each being of constant composition. The limestone is ground to a fine powder, and is mixed in the required proportions with clay in wash-mills to form a thick slurry, which is dried either on heated floors or by the waste gases from the kilns.

Preparation of the Raw Flour for the Kilns—Brickmaking Process.—With rotary kilns no further treatment of the raw materials after grinding is necessary. It is conveyed from the mills to the bins or hoppers supplying the kilns. In the state of flour it cannot be dealt with in fixed kilns, and it is now usual to either pug and wire-cut it or to compress it into bricks. If limestone forms the whole or a considerable part of the mixture this is not an easy process, as the material does not cohere, and the bricks are soft and friable. At an American works using limestone entirely, and making plastic bricks, it is the practice to mix a little natural cement with the flour when pugging. This gives the bricks a slight set, and renders them after drying sufficiently hard to be handled. With materials that are plastic when sufficiently moistened and pugged, wire-cut bricks may be made, but they require drying before they can be burnt. This is usually done in tunnel driers, to which we have referred when dealing with the wet process. With any material we prefer to make semi-dry bricks, as they are denser and more easily handled than if made plastic, and in many cases they may go direct to the kiln without further drying. It is not clear to whom we are indebted for this process, or where it was first employed. It was very fully dealt with by Henry Reid in his book published in 1877, and several types of semi-dry machines were described; but we are not aware whether it was in actual use at the time. We ourselves, after some preliminary experiments with hand-pressing, put it into practice in 1883 on a mixture of lias limestone and shale—a very unfavourable material to deal with, as the flour was entirely wanting in plasticity when wetted. After many failures, we succeeded in producing bricks that were sufficiently dense to bear handling and stacking, and yet not so much so as to be difficult to burn. If too dense, the outside becomes overburnt before the centre has clinkered. The machine used was the Whittaker press, which is largely employed for making semi-dry bricks from shale. Fig. 7 is an illustration of a single die press which will make 500 bricks per hour. It is now used in many cases in this country for preparing raw flour for the kiln, as also are machines of the toggle-lever type. The Dorstenmer hammer press is generally used on the Continent, the brick receiving three blows from a falling hammer. It is important that the flour should be uniformly moistened, and the quantity of water required varies from 9 to 11 per cent., according to the nature of the material and the fineness to which it is ground. The mixing may be done continuously by means of an ordinary paddle-blade conveyor.

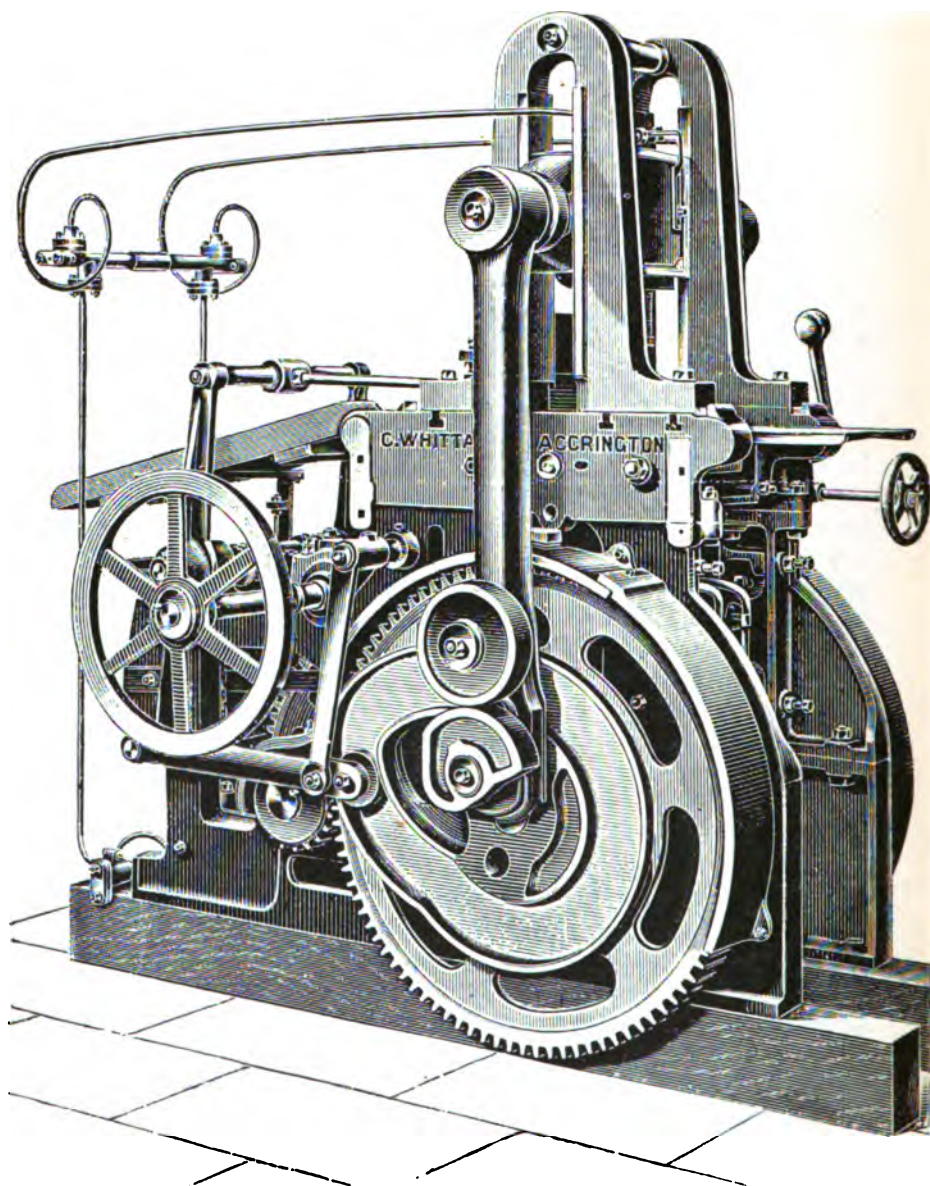


Fig. 7.—Single Die Whittaker Press.

CHAPTER X.

THE DRY PROCESS: CRUSHING, GRINDING, AND AUXILIARY MACHINERY.

CONTENTS.—Crushing and Grinding Machinery—Stonebreaker—The Gyratory Crusher—Grinding by French Burr Millstones—The Ball-mill—The Tube-mill—The Kominor—The Griffin Mill—Spiral Conveyors—Belt Conveyors—The Tray and Swinging Conveyors—Elevators.

Crushing and Grinding Machinery.—From the description given in an earlier chapter it will be understood that only materials capable of being brought into a fine state of subdivision by means of trituration with water are adapted for treatment by the wet process. Many soft materials, however, such as chalk, chalk marl, and certain shales and clays may, by previous drying, be dealt with quite as efficiently by dry methods as by wet grinding. Hard materials must be ground in the dry state, and, with the extended knowledge of cement manufacturers, and the vastly improved grinding machinery placed at their disposal in recent years, the use of such materials for cement making has become very general. The grinding plant in a works using hard limestone becomes an important consideration when it is remembered that, in addition to every 100 tons of cement clinker needing to be ground, about 156 tons of raw material, often of an extremely hard nature, have likewise to be reduced to powder, and that, as is the case in the preparation by wet methods, the grinding must be done with extreme care. It is therefore important that we should deal with the various types of machines that are used at the present time in cement works for crushing, grinding, conveying, and elevating dry materials. It is now very usual to employ precisely the same class of machinery for grinding both the raw materials and the cement clinker, and in many American works using hard limestone for cement making, the grinding plant for the raw materials is an exact counterpart of that employed for grinding the finished cement.

Whatever system of grinding is adopted, preliminary crushing of the material is necessary, and for this purpose the stonebreaker is generally employed. Two types of this machine will require to be considered—viz., the swing-jaw stonebreaker and that constructed on the gyratory system.

The Swing-Jaw Stonebreaker.—Most of these machines are modifications of the original patent of Blake; these modifications consist

generally of different methods of actuating the reciprocating jaw. We can best explain their action by reference to Fig. 8, which is a section of a Blake machine made by Messrs. Robert Broadbent & Son, of Stalybridge. The main frame, A, which carries every part of the machine, consists usually of one casting, which in the larger sizes is strengthened by bolts and steel bands, but which, in the case of machines made for export, is frequently constructed of steel plates, bolted together; X is the swing-jaw shaft, and I the jaw; K¹ and K² are the fixed jaw faces, and J is the swing-jaw face. These faces are of chilled iron or manganese steel, and they are provided with vertical V-shaped grooves which bite into or engage with each other. When worn at the bottom, these parts may be turned end for end, and they will again wear for a considerable time. For the manufacture of

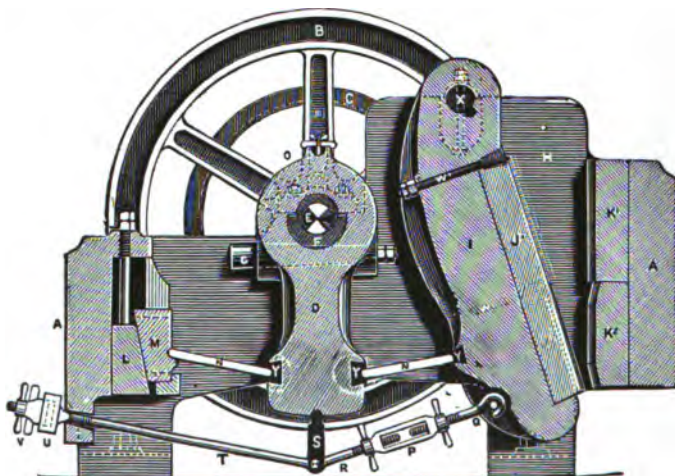


Fig. 8.—Section of Blake Stonebreaker.

road metal, the grooves are large and deep, the object being to break the stone into cubes without crushing it more than is necessary, and to do this with the production of a minimum quantity of small material and dust. When, as in the case of cement manufacture, the object is to crush the material, the grooves are made very much smaller. Thus, for cubing purposes, the distance between the ridges is about $2\frac{1}{2}$ inches, while for crushing the ribs are generally about $1\frac{3}{4}$ inches apart. K¹ and K² are kept in place by the cheeks, H; the swing-jaw face, J, is secured by the wedge-bolts, W¹. E is the driving shaft, the centre portion of which has an eccentricity of about 1 inch. This shaft is provided with two heavy flywheels, B and C, to either of which the driving pulley may be bolted; and by lengthening the shaft a loose pulley can, if necessary, be employed. The eccentric action of the shaft, E, which is driven at a speed of 250 revolutions per minute, imparts a swinging motion to the pitman, D,

and this motion is transmitted by the toggle-plates, N N, to the moving jaw. This jaw approaches to and recedes from the stationary face, and the material to be broken is charged into the hopper-shaped space at the upper part of the jaws. It is thus continuously struck, liberated, and reduced in size as it passes downwards through the gradually contracting opening between the jaws until it is sufficiently small to pass through the

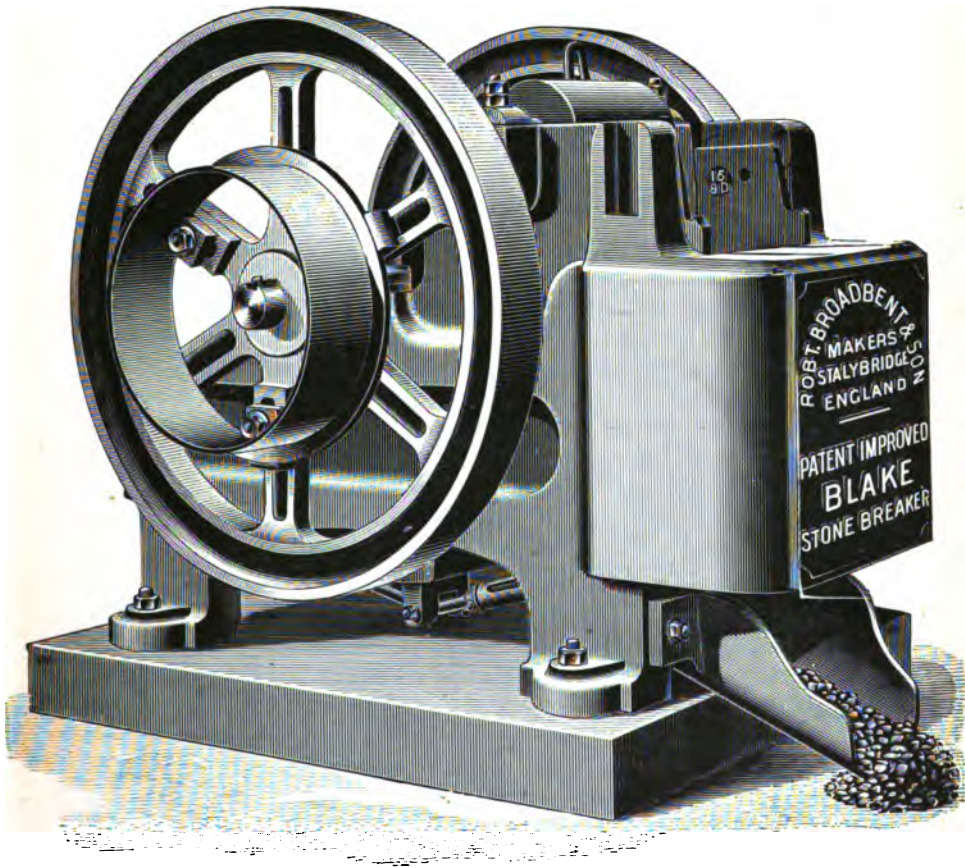


Fig. 9.—Blake Stonebreaker—General View.

orifice at the bottom. The width of this opening is regulated by the wedge block, L, and the return of the swinging jaw is effected by the drawback motion, P, Q, R, S, T, U, V. Any attempt to obtain an extremely fine product at one operation by unduly contracting this lower orifice will certainly result, sooner or later, in the breakage of some part of the machine, and this will probably be the eccentric shaft.

If a fine product is required at this stage it may best be obtained by the use of a second and smaller breaker. The crushed material from the first breaker would in this case be passed through a rotary screen, formed of perforated iron plates, and the portion rejected would then fall between the jaws of the second and smaller machine, which should be set rather closer together than those of the first. The material is thus really sledged at the first operation, during which process a considerable amount of dust and small is made; this dust and small having been removed by the screen, the rejected portion, now of moderate size, becomes further reduced by using a smaller and more closely set machine, without risk of damage. In some cases one machine only is employed, and the product is screened, and the rejected portion, as it is delivered from the end of the screen, is again caused to pass between the jaws; but we consider the use of two machines to be preferable. Fig. 9 is a general view of the Broadbent stonebreaker, which shows the delivery in front. This, however, may be arranged with equal convenience at either side.

The Gyratory Crusher.—The crushing action of the pestle and mortar, where the pestle is simply rotated in the mortar and not used in the form of a stamp, has been taken as the model by more than one inventor for stonebreaking or crushing as also for grinding purposes. Stonebreakers and rough crushers constructed on this principle have long been in very general use in America, and although employed to some extent in this country they have never been popular here. In Fig. 10 we give a sectional perspective view of a machine of this type made by Messrs. Hadfield of Sheffield. It is necessary to understand that the crushing cone, R, does not itself revolve on its axis, but is caused to gyrate. As it gyrates it approaches to and recedes from the shell, N; the distance between the cone and the shell, and consequently the size of the product, being regulated by raising or lowering the central spindle, I, by means of a hand-wheel at the bottom which is not shown in the illustration. The spindle is secured in the required place by the tightening screw, 2. The hollow shaft, to which the crushing cone is firmly attached, is supported on the spindle by the ball and socket bearing, P, 12, and the gyratory motion is imparted to this shaft by the eccentric, G¹. The cone mantle, S, and the concave plates, O, which line the top shell are of Hadfield's manganese steel, and these parts are easily renewable. A special feature of this machine is the arrangement to prevent breakage in the event of the fall of a hammer or a crowbar into the feed opening, which is by no means an unusual occurrence. The driving pulley, J, is not fast to the countershaft, 3, but is free to revolve were it not for its connection to the hub, K, by the two cast-iron break-pins, 13. The hub is keyed fast to the countershaft, and the break-pins are of sufficient strength to drive the crusher when working on the

hardest stone, but they are not strong enough to stand any undue and excessive strain likely to damage the machine.

In comparing the gyratory crusher with the reciprocating jaw machine, it is clear that the efficiency, or output, will depend upon the quantity of the material which can be operated upon in any given period of time, and it is also evident that of these two machines that one will be the most efficient which brings into action the largest effective crushing surface in the time in question. The diameter of the crushing

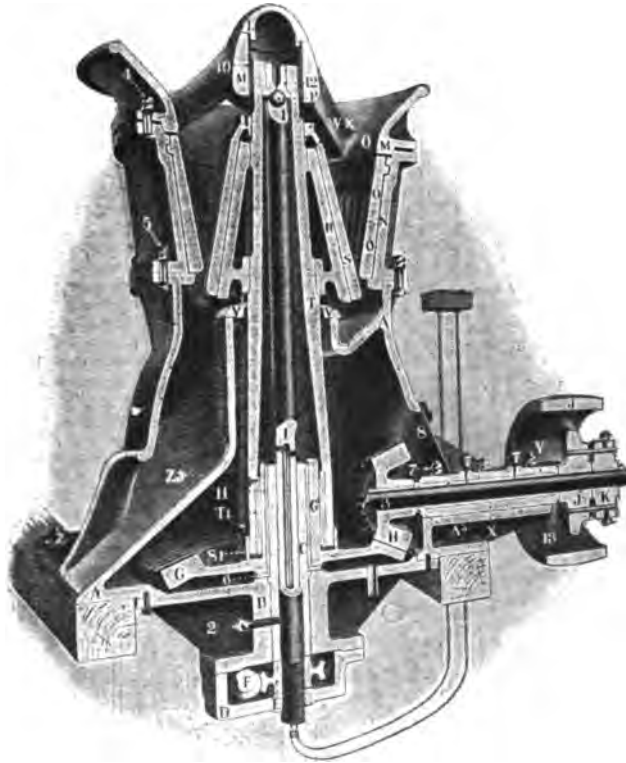


Fig. 10.—Hadfield's Gyratory Crusher.

cone of a gyratory breaker is about the same as the width of the jaw of a reciprocating machine which would admit the same size of stone. As, however, the circumference is about three times the diameter, and as the cone makes one complete gyration for every forward motion of the swinging jaw, it is evident that three times the quantity of material can be dealt with by the gyratory machine in the same period of time as by the machine of the reciprocating type.

Grinding by French Burr Millstones.—This system of grinding is, as regards new installations, now almost obsolete, and for the purpose of grinding cement clinker a few years will probably see the end of all the

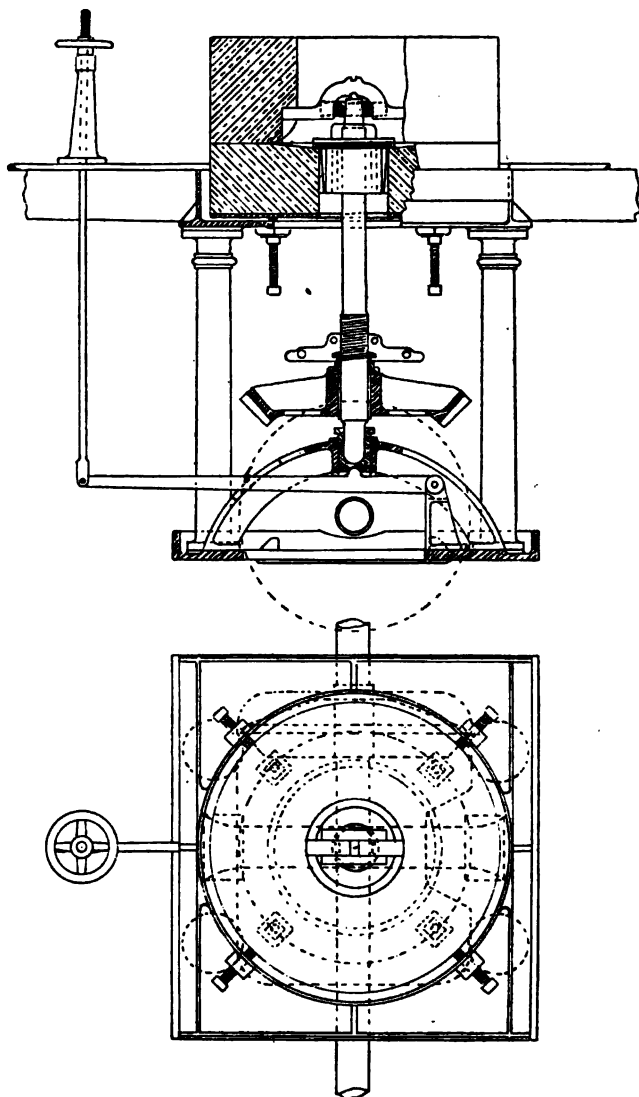
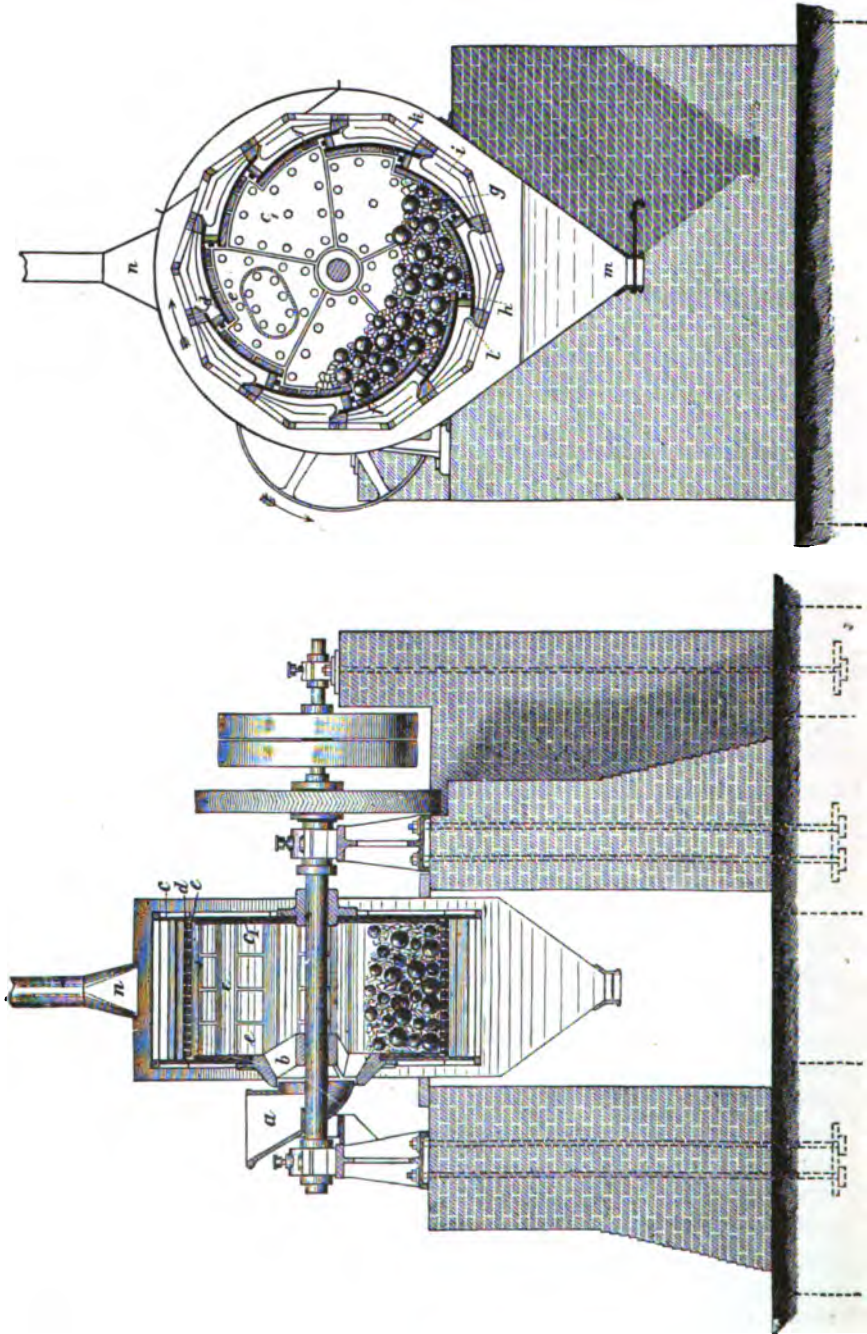


Fig. 11.—Millstones and Driving Gear—Sectional View and Plan.

existing plants. For grinding raw materials, if they are of a soft nature, millstones can, however, be profitably employed and they may be therefore briefly referred to. We have prepared a sectional end view and plan of

one complete hurst (Fig. 11), fitted with stones 4 feet 6 inches in diameter, forming one of a set of seven mills arranged in line and driven from one shaft by nine $1\frac{3}{4}$ -inch ropes direct from the flywheel of the engine. They are grinding moderately hard limestone and clay to produce raw flour, and receive the material to be ground direct from a Blake-type crusher. Our experience, the result of long and careful experiment, goes to show that, contrary to the generally received opinion, nothing is gained by fine crushing the material previous to grinding by this system. The stones make 140 revolutions per minute and the construction of the gearing is extremely simple. The wheels are in halves to facilitate removal, the pinions are both adjusted for working and lifted out of gear by the hand-wheels as shown by the figure. The gearing is easily accessible and is situated in a room below the working floor, away from dust. The lightening gear, for adjusting the stones, is actuated from this floor. The spiral conveyor for collecting the product from the mills is not shown in the figure. It is placed close to the hurst on the wall side, and the cover of the trough is level with the floor; it is thus easily accessible for examination, cleaning, and repairs. The stone cases and the whole of the feed gear are in this installation constructed of wrought iron. On the Continent mills of this type, in which the understone is driven, are used to a considerable extent and are said to give very good results.

The Ball-mill.—This mill is a German invention, and was originally employed for fine grinding, for which purpose, owing to the small output, it did not prove to be an unqualified success. In Fig. 12 we show a transverse and in Fig. 13 an axial section of the mill, as made by Messrs. Jenisch & Lohnert. Its construction has been departed from in some minor details by other makers, but the general principle is the same in all. The machine consists of a rotary drum built up of steel plates on a steel shaft of ample strength, and a feed hopper is provided at one of the sides, which sides are lined with renewable steel or chilled-iron plates. It is made in various sizes up to 7 feet in diameter; each machine requiring a given weight of steel balls of different sizes. A few additional balls are added from time to time to replace loss by wear, as for the efficient working of the mill the specified weight of balls must be maintained. A mill having a drum, 7 feet in diameter and 40 inches wide, revolves at 22 revolutions per minute, and requires about 18 cwts. of balls. The feed is continuous. The inner circumference of the drum is formed of heavy steel plates perforated with $\frac{1}{2}$ -inch holes stepped as shown in Fig. 13; the end of one plate overlapping the beginning of the next one with a space between them. This arrangement has the effect of diverting the balls from their rotary track as the drum revolves, and imparts to them a dropping motion, thereby



Figs. 12 and 13.—Jenisch & Lohnert Ball-mill—Type A.

increasing their crushing and grinding action. Surrounding the grinding plates is fixed a screen of perforated steel plate which forms a protection for the outer or final sieves. These sieves, which are made of perforated metal or brass or steel wire in accordance with the required fineness of

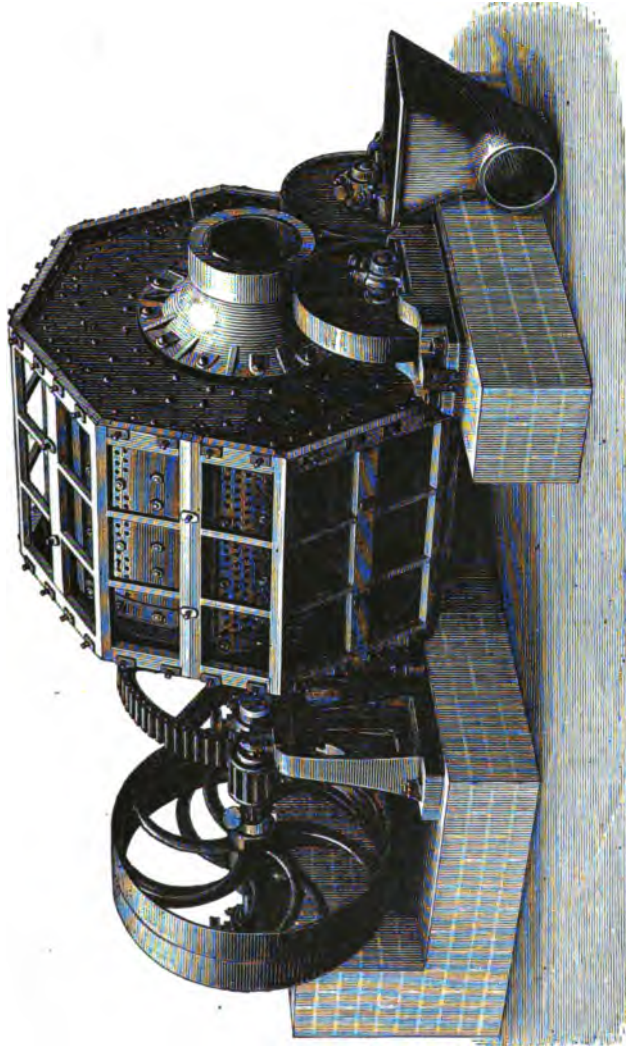


Fig. 14.—Jenisch & Lohnert Ball-mill—Type B.

the product, are constructed so that they can be easily replaced in case of damage. The material acted upon has first to pass through the holes in the grinding plates, then it must traverse the coarse or protecting sieve, leaving only dust and grit to pass to the outer fine sieves. The

portions finally rejected by the sieves fall back to the centre of the drum through the openings between the inner plates for further grinding. The drum is enclosed in a dust-tight iron casing, and the ground material falls into the hopper below in order to be automatically conveyed away. Fig. 14 shows a mill of the same construction as that illustrated in Figs. 12 and 13, except that the shaft instead of passing through the feed hopper terminates inside the drum and is secured to a boss, the external part of which is carried by roller bearings. This allows of the insertion of large pieces of stone and at the same time it enables the diameter of the feed opening to be reduced while admitting of the use of a heavier charge of balls. In a third type of machine the internal shaft and boss are omitted altogether, and the mill is carried by outside bosses resting on roller bearings.

The Tube-mill.—This is a finishing or fine grinding mill for dealing

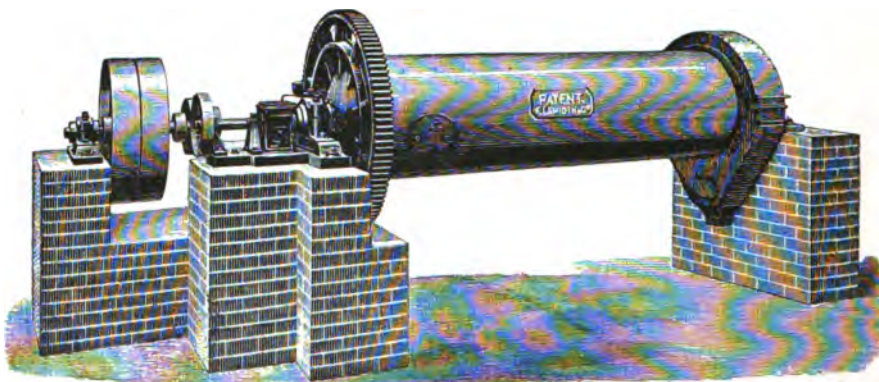


Fig. 15.—Davidsen Tube-mill.

with a product which has previously been coarsely ground by some other means, and was introduced to the cement industry about 1895. This mill, which was the invention of Mr. Davidsen, of the firm of Messrs. Smidth & Co. of Copenhagen, made rapid headway, and it is now used in cement works in every part of the world. The construction of the machine, which is shown in Fig. 15, is simplicity itself. It consists of a long tube or cylinder rolled from steel plate and welded at the joints, being thus entirely without seam or rivet. This cylinder is attached to cast-steel end-plates, provided with pivots, on which it revolves horizontally in bearings lined with anti-friction metal. The pivot at the inlet end is hollow, the material to be ground being delivered through it to the interior of the mill by a worm-feed, either from storage bins or from a hopper containing a small reserve sufficient to ensure steady feeding. The spur driving-wheel is keyed to brackets cast on the inlet-end plate.

The interior of the mill is lined in the case of the smallest size with chilled cast-iron plates; the larger sizes may have similar plates, or they may be lined with quartzite blocks. The diameter of the smallest mill is not sufficient to admit of the use of the latter material. The mill is about half filled with flint pebbles of various sizes, the larger ones being placed near the inlet end; the smaller stones are inserted near the outlet. Delivery of the ground material is arranged for by providing a narrow grid, continued entirely round the circumference of the mill, enclosed by a dust casing. As the mill revolves, the pebbles alternately rise and fall, the grinding being effected by their crushing and rubbing action as the material operated on travels along the cylinder. Loss by wear is made up by the occasional insertion of more pebbles. In new plants the ball-mill, provided with outer sieves of from 20 to 30 meshes to the lineal inch, is now generally employed for the preliminary coarse grinding before the material enters the tube-mill. There is practically no limit to the fineness that may be obtained by the use of the tube-mill, either by finer preparatory grinding, by causing a smaller quantity of material to pass through it, or by the use of several successive mills.

Dimensions and Output.—The Davidsen mill is at present made in the four following sizes, the output from each being compared with that from No. 12, which is taken as unity:—

	Diameter.	Length.	Output.
No. 12, . . .	4 feet, . . .	16 feet, . . .	1.
No. 14, . . .	5 „ . . .	21 „ . . .	2.
No. 16, . . .	5 „ 4 inches, . . .	24 „ . . .	2½ to 3.
No. 17.5, . . .	5 „ 10 „ . . .	27 „ . . .	3½ to 4.

Deviations from the original patent have been made by other makers, but the changes consist principally in details of the method of feeding and in the delivery, which is sometimes arranged at the centre of the end instead of at the circumference. In some of the American machines, the cylinders, instead of being welded, are riveted with butt joints and straps.

The Kominor.—This is a ball-mill of an improved type, especially designed for preparing material for the tube-mill, and it is illustrated in Fig. 16. This machine is the invention of Messrs. F. L. Smidth & Co., and it is known in England by the registered name of “Kominor.” It contains no perforated plates, the material to be operated on is fed in through a hopper at the side, as in the case of a ball-mill, and has to travel across the mill until it arrives at the discharge, which is situated at the periphery on the opposite side to the inlet, exactly as in the Davidsen tube-mill. After passing out, the dust falls upon the sieves, which have a decided slope towards the inlet end, and the portion which does not pass the sieves is conducted back by a series of pipes and is returned to the feed-hopper. It is claimed that besides the crushing

action of the balls they likewise exert a certain amount of rubbing action, due to the passage of the material across the mill, and it is also

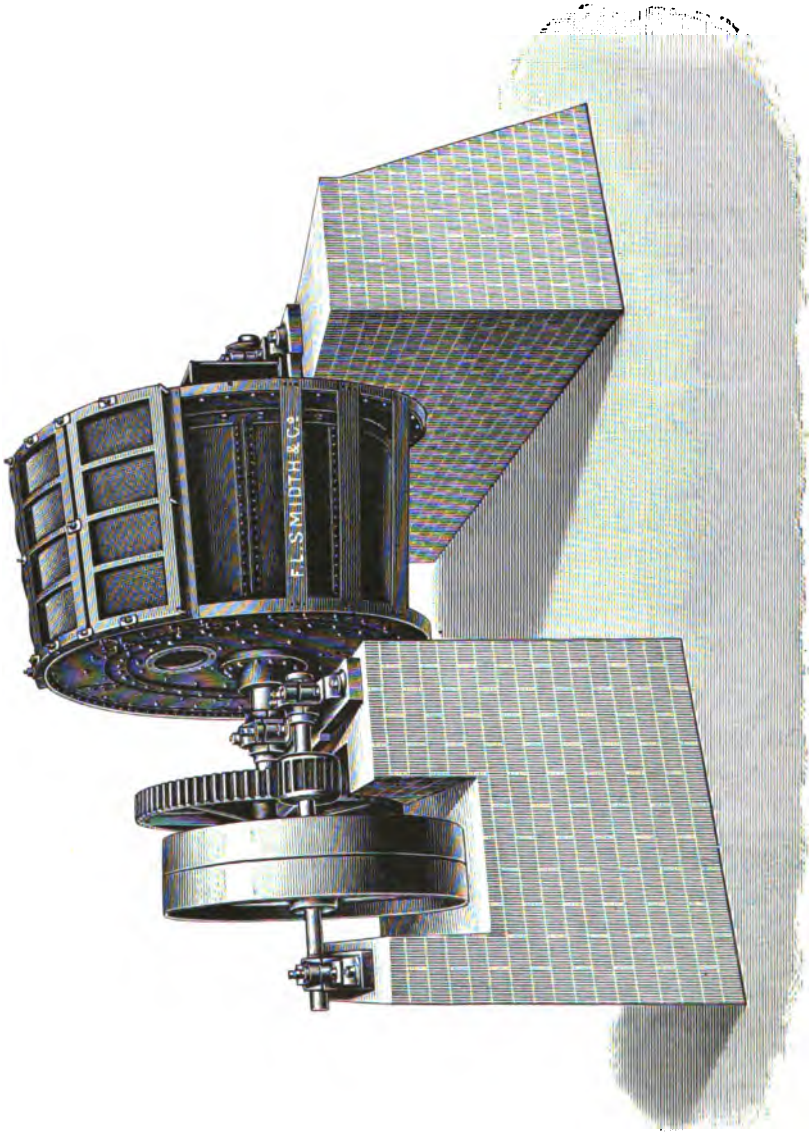


Fig. 16.—The Komino Mill (F. L. Smith & Co.).

asserted that the sloping sieves give a better sifting than the horizontal ones in the old type of ball-mill. A comparative test on limestone between a "Komino" and a ball-mill of equal size was recently made at

a cement works in the Lehigh Valley, Pennsylvania. The limestone was first roughly crushed by a gyrating crusher, some of the pieces fed to the mill being as much as 3 or 4 inches in diameter. The "Kominor" ground 14,000 lbs. per hour, against 8,000 lbs. produced by the ball-mill, both ground to the same degree of fineness, and with no apparent difference in the expenditure of power.

The Griffin Mill.—This is an American mill made by the Bradley Pulveriser Co., and it is shown in elevation and section in Figs. 17 and 18. It consists of a base-plate and pan, 24 (Fig. 18), containing a renewable grinding ring or die, against which the material operated on is ground by the roller, 31. To the base-plate, the sieve frame, 44, is attached, and to this again is fixed the cone, 25, through which the shaft works. The sieve is surrounded by a sheet-iron casing, and in the base-plate are arranged a number of openings outside the grinding ring and pan, through which the finished product falls into a channel below, from which it is removed by a conveyor. Shoes or "plows," which are varied in shape to suit the material operated upon, are attached to the bottom of the roll, and above the roll and in a central position in relation to the sieve a fan, 7, is fixed to the shaft. The driving pulley is horizontal, and contains the universal joint, 9, from which is suspended the shaft, 1, to which the roller is securely fixed. This joint, which is entirely cased in, is the only part requiring lubrication; this is effected through the hole 12.

To quote from the maker's description :—"The roll is revolved within the die in the same direction that the shaft is driven, but when coming in contact with the die it travels around the die in the opposite direction from that in which the roll is revolving with the shaft, thus giving the mill two direct actions on the material to be ground. There is a pressure by centrifugal force of 6,000 pounds brought to bear on the material being pulverised between the roll and die, the united actions being very effective in their combination. The universal joint, by which the shaft is connected to the pulley, allows perfect freedom of movement to the roll, so that it can easily pass over obstructions of any kind. Pieces of iron or steel thus do no damage to the mill."

The feed is continuous through the hopper, 50, by means of the worm, 49, which is driven by the step pulleys, 13 and 40, and which regulate the speed. The mill will deal with material as crushed by a stonebreaker, but passing a $\frac{3}{4}$ -inch ring. As soon as the mill is in full operation, and when sufficient material has entered the pan, it is stirred up and kept in rapid motion by the action of the shoes on the bottom of the roll, which throw it between the grinding ring and the roll. The fine powder, as fast as it is produced, is removed through the screen by the fan, 7, which draws air from the top of the cone, 25; the dust falls into the conveyor channel below. The mill thus continuously grinds and sifts.



Fig. 17.—The Griffin Mill—General View.

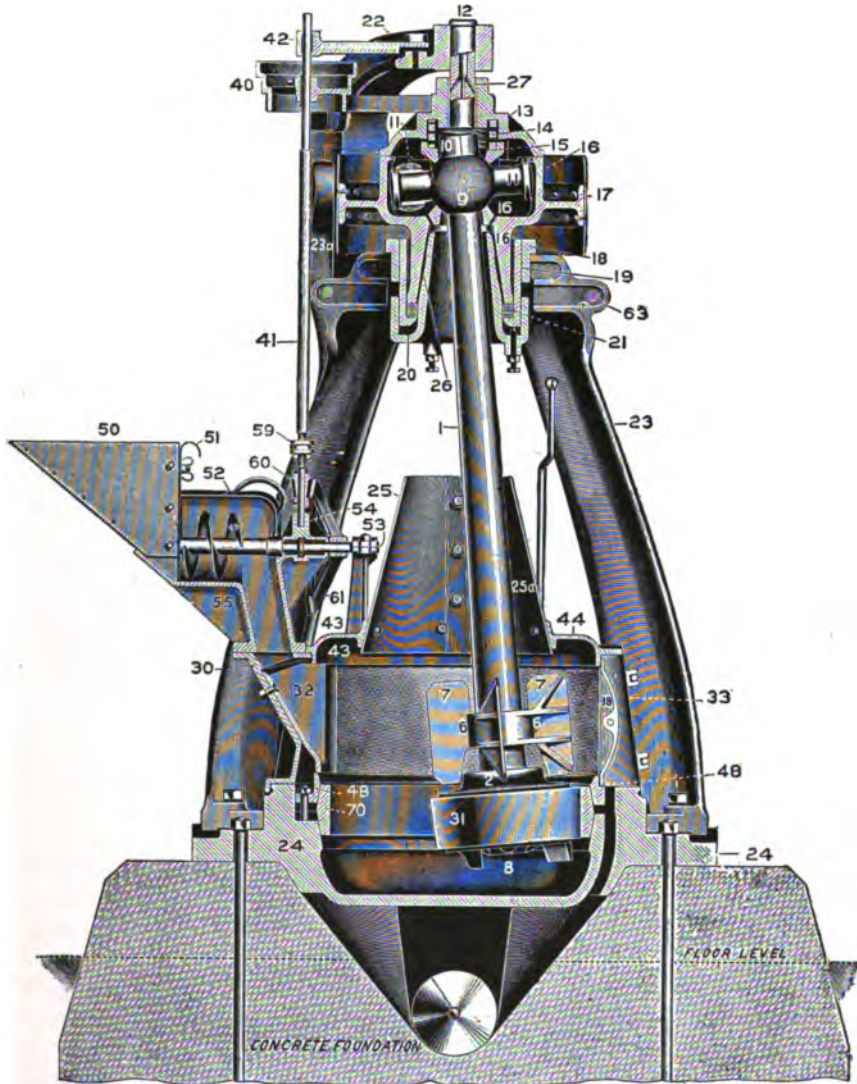


Fig. 18.—The Griffin Mill—Section.

The screen wire may be of much coarser mesh than the finished product. Thus a screen having 16 divisions to the inch will deliver a product leaving less than 10 per cent. of fine residue when tested on a sieve having 60 meshes to the lineal inch. With the ball-mill, the outer sieve must be of the same mesh as the required product, hence the difficulty of obtaining a large output of fine material. The Griffin mill is self-contained, being entirely built on the bed-plate, and by some modifications this mill may be adapted for wet grinding. The diameter of the grinding ring or pan is 32 inches.

Spiral Conveyors.—The employment of the solid cast- or sheet-iron screw-conveyor for the transmission of granular or powdered materials is now almost obsolete. It was found from experiments that the actual work was all done by a narrow portion of the outside circumference of the screw, the remainder of the blade being of no value whatever as

STEVENSON'S PATENT.

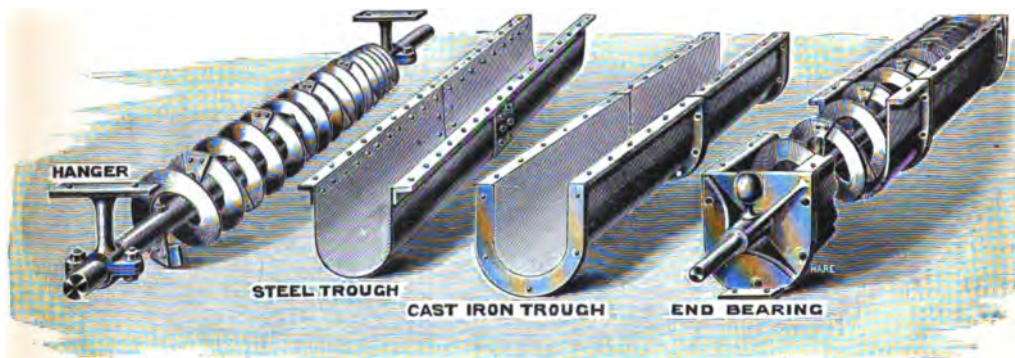


Fig. 19.—Spiral Conveyor.

regards carrying capacity, but really occasioning loss of power by friction. This led to the introduction of the skeleton-conveyor, formed of a strip of steel, coiled by a special machine, to form a spiral of uniform pitch, which is secured to a shaft by steel attachments. One end of these radial attachments is flat, and is bolted to the spiral band, the other end is formed into a split eye, which clips the shaft and is secured by two bolts. The shaft with the conveyor is suspended in troughing, either of cast or of wrought iron, by means of hangers. An illustration is given at Fig. 19 of the conveyor, hanger, and troughing. Delivery may be obtained at any required points by arranging outlets fitted with slides in the bottom of the troughs.

This style of conveyor is well adapted for granular materials or powders in the dry condition. For broken stone or for cement clinker it

is, however, quite unsuitable, and when used for damp materials it does not answer well. This form of conveyor will work satisfactorily on a slightly upward gradient, and it is sometimes convenient to employ it in this way. If the gradient is steep, it is better to utilise a solid conveyor, which will work even up to an angle of 30 degrees; we have not tried it at a greater elevation than this. The spiral conveyor,

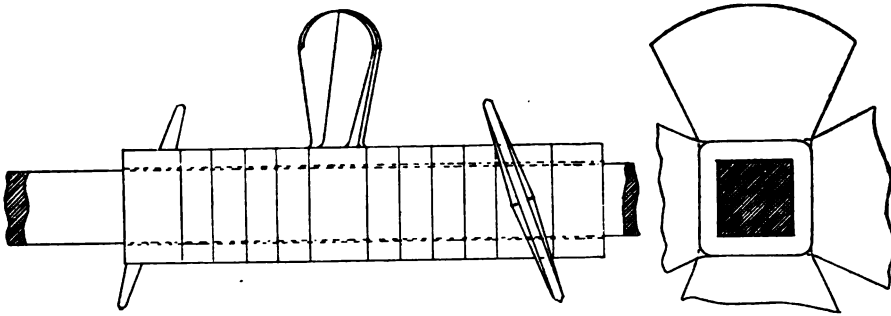


Fig. 20. — Paddle-blade Conveyor.

although very efficient for transport purposes, does not to any great extent mix the material carried. If mixing as well as transmission is required a paddle-blade conveyor should be employed. In Fig. 20 we show one type in which the blades are of chilled iron, and slip on to the square shaft; the blades at the ends and where the hangers occur should

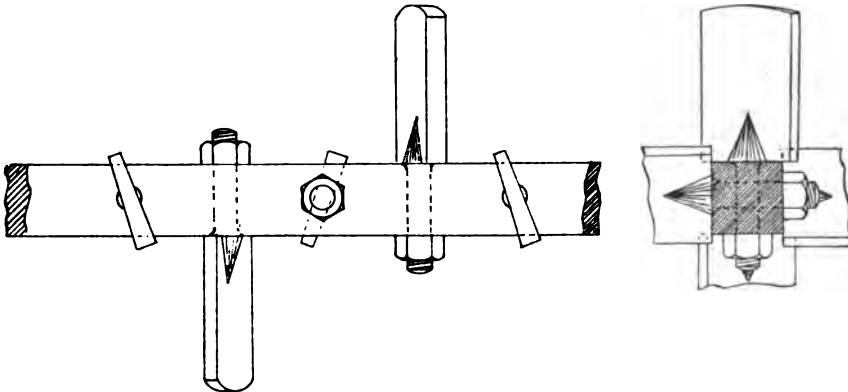


Fig. 21. — Paddle-blade Conveyor (Wedge Cutters).

be secured by set screws. In this type of machine the blades must be made either right or left handed, according to the direction in which the conveyor or mixer is required to deliver. In Fig. 21 the blades are of cast steel, with shanks which pass through the shaft and are secured by nuts. Here it is obvious that by reversing the angle at which they are

set in the shaft the same blades may be used to carry either to the right or to the left hand. A modified form of blade for stiff materials is shown in Fig. 22.

Belt Conveyors.—An endless belt, supported by rollers, will carry almost any material, whether in a coarse or in a fine condition. If required to deliver at a fixed point, the best form of support for the carrying side is composed of three rollers, each of them about equal in length to one-third of the width of the belt. One of these rollers is fixed horizontally under the centre of the belt, and one is placed on either side, with its axis set at an angle of about 45° with the central one. This causes the belt to assume a trough-like shape, and greatly increases its carrying capacity. The rollers should be placed from 4 to 6 feet apart, according to the width of the belt, and the weight of the material to be carried. The empty part of the belt is best supported on flat rollers for the return journey. If it be required to deliver the material at intermediate points, the belt must be flat; it must be of ample width in order

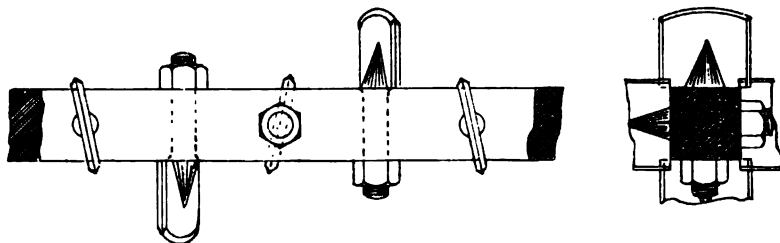


Fig. 22.—Paddle-blade Conveyor (Short Cutters).

to prevent the load from falling off, and it is important that the material should be delivered on to the belt at a uniform rate.

The delivery is effected by means of a throw-off carriage, which runs on the beams passing along each side of the belt in order to support the rollers, and the carriage may be shifted to any position. It effects the stoppage of the stream of material, and it can be arranged to throw it either clear of the belt or into a hopper attached to the carriage, from which it may be led away by shoots. When carrying fine substances, the belt may conveniently travel at a speed of from 200 to 300 feet per minute, and an enormous amount of material may be moved in this way with a very small expenditure of power.

The Tray and the Kreiss Conveyors.—The tray conveyor is illustrated in Fig. 23, which sufficiently explains its construction. It is adapted for carrying broken stone, clay, coke, and materials of this kind, and it is often of value in the re-arrangement of old plants. The Kreiss swinging conveyor consists of an open trough fixed on spring supports, that may either be attached to a floor or may be suspended from above.

The trough is made of very light material, as, contrary to what might be expected, it is subject to but little wear. A shaking motion is imparted to it by a small countershaft and crank, and the material fed in at one end travels quietly and with great rapidity to the other. It may be of any reasonable length (an example is given of one 300 feet long), it may be driven at any point in its length, and it can be lengthened without interfering with the driving mechanism. The conveyor may be fed at any desired point, and the material can be drawn off wherever it is required by means of openings fitted with slides. This conveyor will carry on an upward gradient of 1 in 20, and it is claimed for it that it will convey any material, fine or coarse, either in a dry or in a damp condition. It requires but little power to drive; a conveyor driven by a belt 2 inches wide running on a pulley 6 inches in diameter will convey 7 tons per hour. Our own knowledge of it is confined to its use

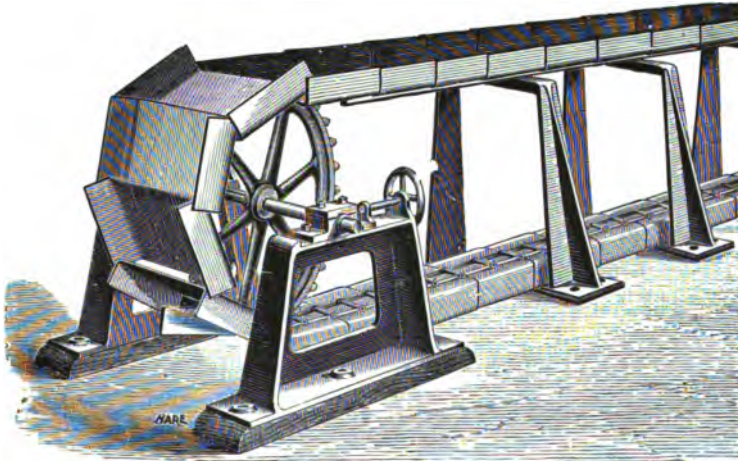


Fig. 23.—The Tray Conveyor.

for transporting broken stone, for which purpose it proved to be admirably adapted.

Elevators.—These, when used for the purposes under consideration, consist of endless belts or chains travelling over pulleys or wheels, to which are attached at regular intervals buckets which lift and deliver the material to be elevated. The buckets are now usually stamped from steel plate, without seams or overlapping edges, and with round corners to facilitate delivery. They may be obtained in an almost endless variety of patterns as regards shape, capacity, and thickness of plate. Textile belting is frequently employed for elevators, the buckets being attached to the belt by means of flat-headed bolts, as shown in Fig. 24, the belt being arranged to run over ordinary pulleys.

Detachable link chains of steel or of malleable iron, with suitable links to which the buckets can be attached, may be obtained in many forms and sizes. Examples are given in Figs. 25 to 28. In Fig. 29 is shown the sprocket wheel at the head of the elevator, by which the chain is carried round the shaft. Fig. 30 illustrates a complete vertical elevator without the casing, and Fig. 31 shows an inclined elevator fully cased in. It will be noticed that means are provided in the bottom fixing or boot for taking up the wear of the chain or belt.

It is necessary that the feed to elevators should be uniform, and, if possible, it should always be at the front or up side, so that the material may fall into the rising buckets, instead of being entirely scooped up, as must be the case if they are fed at the back. This apparatus should always be driven from the top. As to the respective merits of belts or chains, every case

must be specially considered on its merits. Without doubt all the products of the various stages of the manufacture of cement may be lifted by belt elevators, and if the lifts are high, and if the elevators are inclined from the perpendicular, belts should be employed on account of their lightness. In highly inclined belt elevators, the upsides should run on a board, the down side being allowed to hang free. The belt may then run fairly slack. For high lifts the pulleys



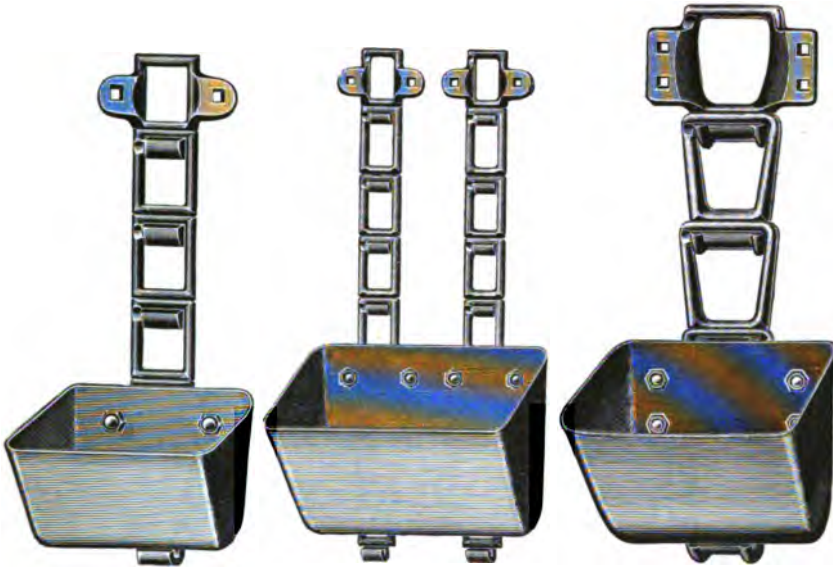
Fig. 24. — Detail of Belt Elevator.



Fig. 25. — Details of Chain Belt and Elevator.

for belt elevators should always be flanged.

In the case of raw flour it is best to employ belts, and a cotton belt will last for this purpose for many years. On the other hand, cement powder is very destructive to belts of this nature, and chain belts will be found to be more durable for ground cement. The same advice may be given in the case of cement clinker, while there is here the additional risk of damage likely to be caused by hot lumps of the material. For damp raw flour nothing stands better than a solid woven cotton belt, well pickled in a preservative solution.



Figs. 26, 27, 28.—Details of Chain Belt and Elevators.



Fig. 29.—Detail Showing Head of Elevator.



Fig. 30.—Vertical Chain Belt Elevator.

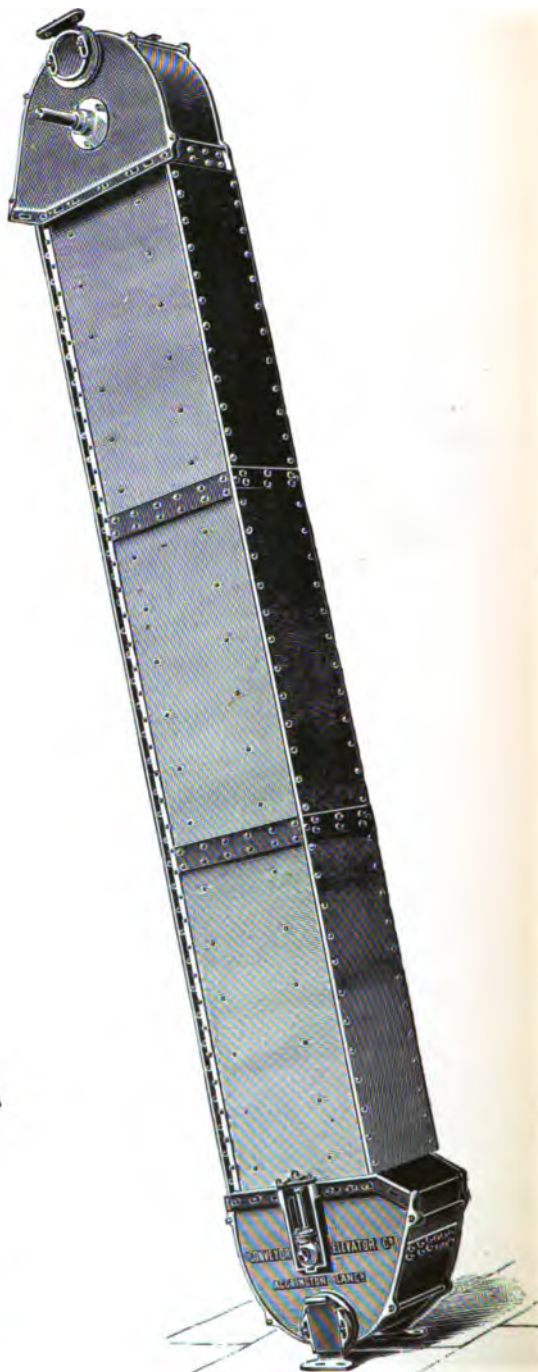


Fig. 31.—Inclined Elevator, Cased in.

CHAPTER XI.

THE CALCINATION OF THE CEMENT MIXTURE.

CONTENTS.—Chemistry of Cement Calcination—Fremy's Experiments—Exclusion of Sulphur—Alumina and the Setting Process—Landrin's Experiments—Substances found in Cements—M. Le Chatelier's Experiments—Microscopical Investigations—Dr. Erdmenger's Experiments—Messrs. Newberry's Experiments—Calcination in the Open Kiln—Closed Kiln—The Johnson Chambers—Gibbon's Chambers—Michele's Chambers—Batchelor Kiln—Drying Chambers for Bricks—Gases Evolved from Cement Kilns—Shaft Kilns—Dietsch Kiln—Aalborg Kiln—Schneider Kiln—Hauenschild Kiln—Hotop Kiln—Stein Kiln—Hoffmann Kiln.

Chemistry of Cement Calcination.—We have already spoken of the chemical changes which have to be effected in the kiln—firstly, the expulsion of the carbonic acid gas, which is a matter of no difficulty; and secondly, the production of compounds of silica, lime, and alumina at a point very little short of that of fusion. The lime, on being freed from its carbonic acid gas, and, therefore, in what is termed the "nascent state," is in the best possible condition to enter into fresh combinations. As the temperature in the kiln rises the draught increases, and the sluggish and heavy carbonic acid gas is by degrees passed out of the kiln. The free lime is then presented to the silicate of alumina of the clay, and, as laboratory experiments prove, it is enabled to expel the alumina and to form a fairly stable base, the calcic silicate, but in the proportions found by experiment to be those best adapted for the production of Portland cement, there is invariably a much larger amount of lime present than the silica alone can neutralise. The alumina assumes at very high temperatures acid functions, and enters into combination with a further portion of the lime to form the so-called aluminate of lime. The same may be true to some extent also of the iron.

Fremy's Experiments.—M. Fremy, whose experiments are relied upon to prove the existence of this alumina compound in Portland cement, was able to produce a base from lime and alumina alone in the absence of silica, and he thus dispelled the theory that the alumina still continued in combination with the silica in the form of the double silicate of lime and alumina.

In order to obtain the alumina in a perfectly pure state, M. Fremy, whose researches were first published in 1865, prepared this substance by the calcination of ammonia alum. He also produced lime of absolute

purity from Iceland spar. When this latter material is submitted to the intense heat of the wind furnace the resultant lime does not melt, but is transformed into a crystalline substance with a cleavage resembling that of marble.

Precautions taken to exclude Sulphur.—The experiments with lime and alumina were carried out in carbon crucibles, and in order to avoid the possibility of the formation of calcium sulphide, due to impurities in the fuel, the mixtures of alumina and lime were placed in a small inner carbon crucible, enclosed in an outer one packed full of powdered lime. In the utmost heat of the wind furnace, mixtures of 80 parts of lime and 20 of alumina were melted, as were also mixtures containing 90 parts of lime and 10 of alumina. A mixture of 93 parts of lime and 7 of alumina was even fritted or run to glass. The alumina, in fact, serves as an excellent flux for the lime, and in this respect is superior even to silica. These compounds of lime and alumina, containing such a large excess of lime, are crystalline in structure; indeed, their fracture resembles that of loaf sugar. They have a strongly alkaline reaction, and combine with water with a considerable evolution of heat. They may in some respects compare with fluxed lime. These substances, which swell up in water, however, like quicklime, can obviously play no part in the set of cements; but the case is quite different when we have to deal with compounds of lime and alumina, represented by the formulæ $\text{CaO}, \text{Al}_2\text{O}_3$, $2\text{CaO}, \text{Al}_2\text{O}_3$, and $3\text{CaO}, \text{Al}_2\text{O}_3$, which are less basic than the foregoing salts. When these aluminates are reduced to a fine powder and gauged with water, they at once solidify and form hydrates, which acquire, even in water, a considerable degree of hardness; they are, moreover, capable of binding together large quantities of sand to form hydraulic mortars, which have a stone-like consistency.

Part taken by Alumina in the Setting Process.—As the outcome of these experiments, M. Fremy was led to assert that the set of cements was caused by the hydration of the aluminates of lime, and not by that of the compounds of lime and silica, which had no setting action, nor by the double silicates of lime and alumina, which in all different proportions he found to be likewise inert. If the accuracy of these investigations be admitted, we must relinquish all those theories of cement action which depend for their explanation on the behaviour of compounds of lime and silica.

Further Experiments by M. Fremy.—The setting action of the compounds of lime and alumina was not, however, sufficient to explain all the phenomena of hydraulicity, as M. Fremy himself recognised, for it would not account for the behaviour of quicklime in the presence of puzzuolana or of a calcined silicate of alumina. In a subsequent memoir, in 1868, he showed that even in the case of a perfectly pure hydrated

silicate of alumina, which contained 65 per cent. of silica, 25 per cent. of alumina and 10 per cent. of water, and was represented by the formula $3(\text{SiO}_2)\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, an excellent puzzuolana could be produced by simple calcination at a temperature of about $1,300^\circ \text{F}$. This substance, on the addition of water, was able to impart to lime hydraulic properties which were manifestly due to the simple dehydration of the clay, and it was found by further experiment that pure hydrated silicates of alumina, even when intensely heated, still retained their power of recombining with water and acting as puzzuolana; the only difference being that after exposure to very high temperatures the setting action of the mixture of lime and clay was retarded. The interval needed for induration could be extended or decreased in accordance with the temperature at which the silicate was calcined. He states his belief that all clays capable of acting as puzzuolanas, or such as contain relatively large quantities of silica which become gelatinous when treated with hydrochloric acid, are decomposed by dehydration; that a certain proportion of the combined silica and alumina is not only decomposed, but that these elements remain separated and are present in an allotropic form; they are thus ready to form new compounds when presented to quicklime in the presence of water. There are, however, as he points out, many puzzuolanas which contain also notable quantities of lime, in addition to the silica and the alumina, and in these substances the effect of calcination is to bring about the formation of fresh compounds of lime and the silicates, in addition to the free silica and alumina, which substances are capable of re-arrangement in the presence of water. He regards Portland cement then as a highly complex body, which must comprise aluminates of lime formed at extreme temperatures, but also notable proportions of these puzzuolana-like substances, all of them capable of becoming indurated in the presence of lime after treatment with water.

M. Landrin's Experiments on Cements.—Some important observations upon the silicates of lime have been communicated to the *Académie des Sciences* by M. Landrin, another patient investigator, who has done much to throw light upon this vexed question. He believes that in the compound of 44.55 parts of silica with 55.45 parts of lime, a salt which has the formula of $5\text{CaO}, 3\text{SiO}_2$, we have the basis of all good Portland cements. He terms this substance "pouzzo-Portland," because it is found to exist alike in Portland cement and in puzzuolana. It would seem from his experiments that it constitutes a large proportion of all cements of the Portland type, along with aluminates of lime, oxide of iron, and magnesia. It has been observed that when equal quantities of lime and silica, in a pure state, are strongly heated, a compound is obtained resembling Wollastonite, with the formula CaO, SiO_2 , which contains 48.4 of lime and 51.4 of silica. This substance, which is very hard and crystalline in

fracture, is not attacked by water, and thus is not capable in any way of influencing cement action. If the volume of lime is doubled so as to obtain a compound answering to the formula $2\text{CaO}, \text{SiO}_2$, containing 65.1 per cent. of lime and 34.9 per cent. of silica, the resulting silicate is, when hot, a hard compact mass, but as it cools it gradually disintegrates and crumbles away into a bulky grey powder, rather resembling slaked lime. This is no doubt the substance, also termed the ortho-silicate, which is present in so-called "slippy clinker," produced from over-clayed slurry.

M. Le Chatelier's Experiments with the Microscope.—This theory, which is very ingenious, and not incapable of being reconciled with the views of Feichtinger and other chemists, received much confirmation from the more recent investigations of M. Le Chatelier, which were communicated to the Paris Academy on March 22nd, 1882, by M. Daubree on behalf of M. H. Le Chatelier, whose investigations were temporarily suspended. This latter savant has pursued his investigations by means of the polariscope. He finds on cutting thin sections of Portland cement clinker that the mass is composed undoubtedly of a variety of chemical compounds. It is quite impossible to isolate each of these small particles for analysis, but he has been able by synthesis to build up from lime, silica, and alumina the different bodies which he recognises as forming part of the clinker, and he has ascertained that these substances, when viewed with polarised light in the microscope, are really the compounds he finds in the clinker.

Principal Substances present in Cement.—The following are among the chief bodies present in Portland cement:—

1. A substance which has no action on polarised light. It consists of aluminate of lime, rich in lime, occasionally mixed with particles of free lime. M. Le Chatelier actually produced by artificial means a tricalcium aluminate, $3\text{CaO}, \text{Al}_2\text{O}_3$; he assured himself that this salt crystallises in the cubic, consequently polariscopically inactive, system, and that, moreover, it is the only possible compound of lime capable of being present in cements, besides lime itself, which crystallises in this system.

2. A substance acting feebly on polarised light and presenting a clearly-defined crystalline form. This is a silicate of lime. M. Le Chatelier perceives in this the chief, if not the only active, ingredient of cements; this substance always constitutes the principal part and sometimes the entirety of Portland cements. He believes himself in a position to affirm that it is a calcareous peridot (lime olivine), $2\text{CaO}, \text{SiO}_2$, which, upon the calcination of the cement, crystallises in the matrix described in the next paragraph, when the whole is carried to the point of fusion.

3. A substance, having a deep brown colour, which acts upon polarised light. This is the most fusible of the components of cements. It constitutes in the solid form the gangue of the silicate which has just been

described, and when melted it is the cause of its crystallisation. It is an aluminoferrite of lime, having less lime than the tricalcium aluminate. M. Le Chatelier assigns to it the formula $2(\text{AlFe})_2\text{O}_3 \cdot 3\text{CaO}$. He was able to produce synthetically a compound answering to this formula, and found it to possess the optical characteristics and the ready fusibility of the similar substance present in cement. This material is slowly acted upon by water, and is but little changed during the setting process.

4. Small crystals having a very energetic action upon polarised light. These are by no means numerous, and undergo no change upon coming in contact with water. These are probably magnesium compounds, since M. Le Chatelier has ascertained that all very basic calcareous compounds are acted upon by water in contradistinction to those of magnesia.

Microscopical Investigations upon the Setting Process.—In examining the setting action of cements under the microscope by means of polarised light, M. Le Chatelier discovered that the addition of water leads to the formation of several different compounds. Of these the most important, as respects the induration, is a substance which crystallises in hexagonal laminae, resembling the crystals of calcium hydrate, but he was unable to collect them in sufficient quantity to determine their composition. Whatever it may be, this material is undoubtedly a derivative of the calcium ortho-silicate. In quick-setting cements which are rich in alumina, there is a copious formation of long acicular crystals which interlace in all directions. These crystals, when exposed to dry air, become dehydrated and shrink greatly in volume; if heated in water to a temperature of 50°C . they break up into fragments. They are produced by the action of water on tricalcium aluminate, which is slightly soluble in pure water, but more so in salt water, in which latter the crystals become partly decomposed. It may be the disruption of these crystals in certain defective qualities of Portland cement which causes the failure of the concrete in sea-water.

The Causes of "Creeping" in Cement Clinker.—In the course of his experiments he discovered several other substances which did not act upon polarised light, but he was unable to find that they played any part in the setting process. He, however, ascertained that the calcium ortho-silicate before mentioned gave rise to the peculiar action of "creeping," above alluded to, often noticed during the process of cement manufacture. Heated to the point of fusion and then allowed to cool gradually, this substance at first took the form of a stone-like semi-translucent mass, which, however, crumbles into a powder, composed of fragments of minute twinned crystals, as it cools. This action is undoubtedly due to unequal tension on the opposite faces of the twins. If the compound is less intensely heated the twins are not formed and no disruption takes place.

Dr. Erdmenger's Experiments on Clinker that Spontaneously Disintegrates.—Cement from this clinker although it ultimately hardens is always of low strength. If the hot clinker is quenched with water, disintegration does not take place, and Dr. Erdmenger has shown the effect of this treatment on the resulting cement.* Tests were made from four samples of cement all containing 61 per cent. of lime. No. 1 was from normal clinker which did not disintegrate; No. 2 from overburned clinker which disintegrated spontaneously; No. 3 from similar clinker which was cooled by a stream of water and remained sound; and No. 4 from similar clinker thrown while hot into cold water which granulated it, the granulated clinker being dried before grinding. The following are the results in lbs. per square inch, 1 part cement to 3 parts sand :—

	1.	2.	3.	4.
Two days,	128·0	64·0	118·1	113·8
Three days,	160·7	71·1	133·7	142·0
Seven days,	243·3	113·8	213·4	246·1
Twenty-eight days,	358·5	195·0	322·9	342·8
Three months,	442·5	239·0	398·3	435·3

M. Le Chatelier's Recent Experiments.—The results of M. Le Chatelier's most recent work in this direction were published in the *Annales des Mines*, 1887, pp. 388 to 412. In addition to a microscopic examination of cement, both in the form of clinker and after setting and hardening in water, he prepared various silicates, aluminates, and ferrites of lime by heating mixtures of the pure materials. Generally his conclusions are as follows :—

The mono-calcium silicate, CaO, SiO_2 , is unacted upon by water, and can therefore if present contribute nothing to the hardening of cement.

The di-calcium silicate, $2\text{CaO}, \text{SiO}_2$, obtained by heating lime and silica, forms while hot a hard compact mass, which disintegrates and falls to powder on cooling. To the presence of this silicate the above spontaneous disintegration of clinker when taken hot from the kiln is attributed.

The tri-calcium silicate, $3\text{CaO}, \text{SiO}_2$, is the one to which the hardening of Portland cement is due. This cannot be prepared by direct fusion of its constituents, but may be produced indirectly by fusing lime with a silicate.

The three aluminates $\text{CaO}, \text{Al}_2\text{O}_3$, $2\text{CaO}, \text{Al}_2\text{O}_3$, $3\text{CaO}, \text{Al}_2\text{O}_3$, all set with water, and thus it is to their presence that the initial setting of cement as distinguished from its ultimate hardening is due.

The ferrites corresponding to the aluminates in which the alumina

* *Thonind. Zeit.*, 1893, vol. xvii., p. 238.

is replaced by ferric oxide slake on the addition of water and do not set.

On these results Le Chatelier based the formula, we have already given, for calculating the proportion of lime to silica and alumina taken together in Portland cement, any magnesia present being considered as equivalent to lime.

Messrs. S. B. and W. B. Newberry's Experiments on the Constitution of Hydraulic Cements.—The results of these experiments were communicated to the New York section of the Society of Chemical Industry.* Working by synthesis with pure materials in an extremely fine state of division, very perfect mixtures of known composition were made of carbonate of lime with silica, alumina, oxide of iron, and magnesia respectively, which were burned in a Fletcher gas furnace with gasoline gas. A quantity of about 300 grammes of the mixture was taken for each experiment, the resulting products being ground and gauged with water; the hardening properties were then noted, and the soundness or constancy of volume was determined by the hot water test. Messrs. Newberry obtained the tri-calcium silicate, $3\text{CaO}, \text{SiO}_2$, by direct union of lime and silica which Le Chatelier failed to produce in this way. They also found that the tri-calcium aluminate, $3\text{CaO}, \text{Al}_2\text{O}_3$, when powdered and mixed with water cracked after setting, and entirely disintegrated when placed in water. The general conclusions arrived at by them were as follows:—

1. "The essential constituents of Portland cement are tri-calcium silicate with varying proportions of di-calcium aluminate. This composition may therefore be expressed by the formula $X(3\text{CaO}, \text{SiO}_2) + Y(2\text{CaO}, \text{Al}_2\text{O}_3)$. From this formula it may be calculated that the correct proportion of lime, by weight, in Portland cement, is 2.8 times the silica plus 1.1 times the alumina."

2. "Iron oxide combines with lime at a high temperature, and acts like alumina in promoting the combination of silica and lime. For practical purposes, however, the presence of iron oxide in a clay need not be considered in calculating the proportion of lime required."

3. "Alkalies, so far as indicated by the behaviour of soda, are of no value in promoting the combination of lime and silica, and probably play no part in the formation of cement."

4. "Magnesia, though possessing marked hydraulic properties when ignited alone, yields no hydraulic products when heated with silica, alumina, or clay, and probably plays no part in the formation of cement. It is incapable of replacing lime in cement mixtures, the composition of which should be calculated on the basis of the lime only, without regard to the magnesia present."

* *Journ. Soc. of Chem. Ind.*, vol. xvi., 1897, pp. 887 to 894.

We may now proceed to treat of the practical processes of manufacture.

Calcination in the Open Kiln.—This was the type of kiln originally employed, and its design was evidently based upon that of the lime kiln, but in addition it was surmounted by a tapering chimney or cone to increase the draught. The capacity generally varies from 20 to 30 tons of burned material, the larger size being slightly more economical of fuel. The bottom is provided with a grate of loose bars, upon which alternate layers of coke and dry raw material are laid until the kiln is filled. It is then lighted, allowed to burn off, and when cold the charge is withdrawn. While extravagant as regards the item of fuel consumption, this type of kiln produces clinker of excellent quality. The results of some of our own experiments to determine the exact weight of fuel used per ton of clinker burned in open kilns of 20 tons capacity were as follows:—The material burned was wet process slurry, well dried on flats. It contained 76 per cent. of carbonate of lime, was of uniform composition, and as it left the wash-mill was of such fineness that it entirely passed through a test-sieve having 10,000 meshes to the square inch. It was specially well dried for these trials, and was found on the mean of several determinations to contain 2 per cent. of water only. The coke also was fairly dry. Pieces of moderate size were employed, except in the bottoms, for which larger lumps were picked out. Five brushwood faggots were used in each case to start the fires. In kilns Nos. 3 and 7 all the materials were accurately weighed in and the product was weighed out.

The weight of coke was in No. 3 kiln—

In bottom on faggots, . . .	0 tons	7 cwts.	1 qr.	24 lbs.
In layers interstratified, . . .	7 "	4 "	0 "	20 "
On top of kiln, . . .	0 "	7 "	0 "	0 "
Total, . . .	7 tons	18 cwts.	2 qrs.	16 lbs.

This kiln yielded 19 tons 2 cwts. 2 qrs. of good clinker, and 6 cwts. 3 qrs. of yellow; and, therefore, to produce 1 ton of clinker, the coke required was 8 cwts. 1 qr. 5 lbs. As the mean of repeated observations, 50 bushels of gas coke fresh from the works weigh 21 cwts., and, therefore, 8 cwts. 1 qr. 5 lbs. are equal approximately to $19\frac{1}{4}$ bushels. The coke cost $2\frac{1}{2}$ d. per bushel, and, therefore, the cost of the coke for burning 1 ton of cement was almost exactly 4s.

In No. 7 kiln, with the same careful observations, 7 tons 17 cwts. 2 qrs. 16 lbs. of coke produced 19 tons 7 cwts. 2 qrs. of clinker, and 2 cwts. 1 qr. 12 lbs. of yellow; the coke used per ton of clinker was thus 8 cwts. 15 lbs., say, $19\frac{1}{2}$ bushels, costing about 4s., as before.

In a third trial, the weights in which were arrived at by an average,

each ton of clinker needed 18·66 bushels of coke, or, say, 3s. 11d. per ton, for the fuel for burning.

The Closed Kiln.—Open kilns are now rarely employed. While the shape of the burning portion remains practically unchanged, the open tops are dispensed with, the products of combustion being by various arrangements made to dry sufficient material for the succeeding charge. Kilns of this type are in very general use in this country for dealing with the slurry of the wet process, which is lifted and distributed by pumps upon the floors of the drying chambers. Some of those most generally employed will be briefly described.

The Johnson Chambers.—The plan patented by Mr. Johnson consists merely in the addition to the kiln, at or about the top level of the cup-shaped portion, of an arched chamber of the same width as the kiln, and of such a length that the floor area will hold enough of the wet slip to serve when dry as the charge of the next kiln. As will be seen from our illustration (Fig. 32) this chamber is simply a short tunnel, interposed between the kiln and the chimney, and each chamber may be from 12 to 14 feet in width by from 80 to 100 feet in length. The dimensions will depend upon the size of the kiln and the height of the chimney. The floor is slightly inclined, falling towards the kiln, so that the stratum of slurry may be deepest where the greatest heat is found in the vicinity of the kiln; the depth of the layer of slurry may vary from 10 to 12 inches, close to the kiln, to about 3 or 4 inches at the far end of the chamber. The use of these chambers involves a considerable extra chimney power, and lofty chimneys must be erected to produce the best results.

Sulphur Deposits on Surface of Slurry.—An objection which has been raised against this plan is that with some descriptions of slurry there is a very considerable deposit of solid particles, chiefly sulphur compounds, upon the surface of the matters in the chambers. The hot gases passing out of the kiln are condensed when they come in contact with the cold slurry, and we have seen in some cases the whole surface heavily coated with such a deposit. The best answer to this objection is that no permanent injury is caused to the resultant cement, as nearly all this matter will again sublime when it comes into the kiln, and is exposed to the full heat during the process of burning.

Fuel used with Johnson's Chambers.—As compared with our own experiments with open kilns we may place the facts kindly communicated by Mr. Johnson on this subject. He states that the cost of fuel for the drying of the slip into slurry, and used in the kilns on his system, amounts to 5s. 3d. per ton of the finished cement. If to our figures we add 1s. per ton for the cost of fuel required to dry the slurry, we obtain an estimate which compares fairly well with that of Mr.

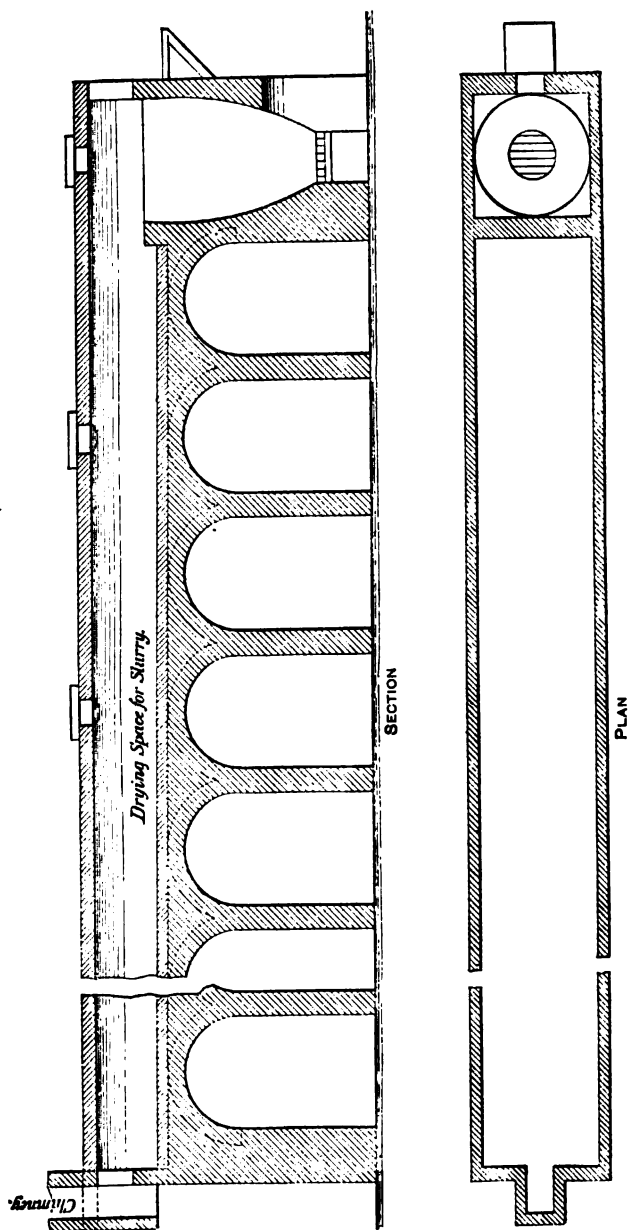


Fig. 32.—Johnson's Drying Chambers.

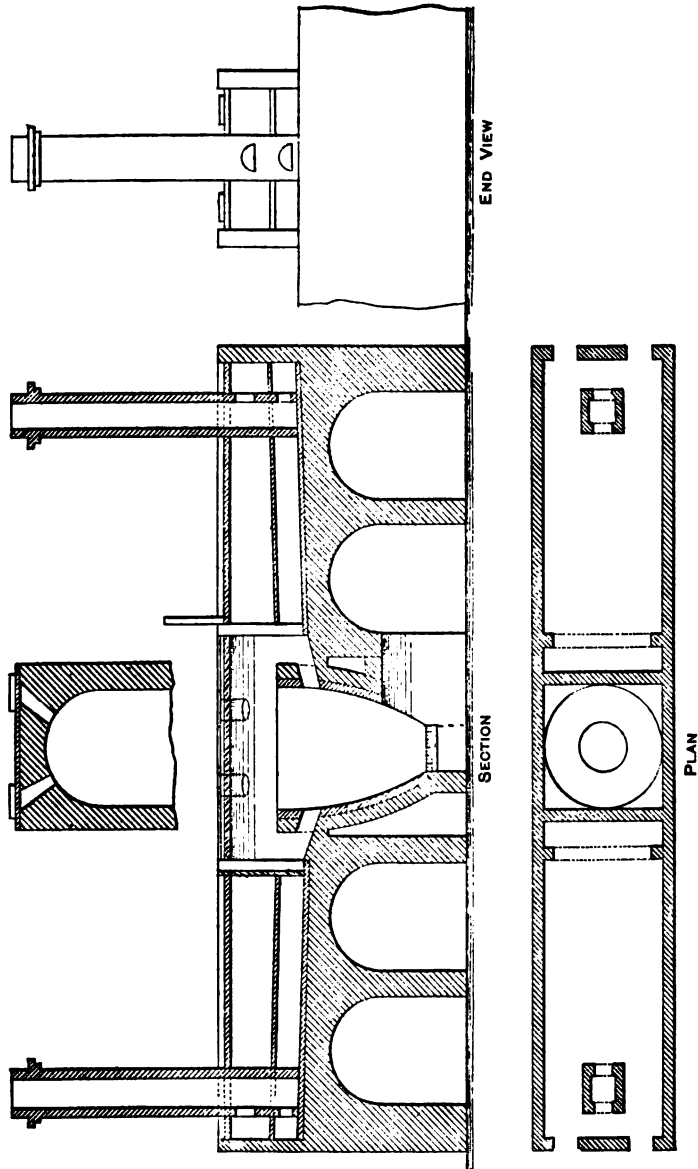


Fig. 33.—Gibbons' Patent Chambers.

Johnson. But Mr. Johnson's totals, based on the working under the old system of kilns of large size, partly fired with gas coke, but in the main (to the extent of two-thirds) with coke made in ovens beneath the drying floors, show a much larger cost. He estimates the expense of the gas coke and oven coke for burning 133 tons of cement clinker as follows:—

50 chaldrons of coke-oven coke, at 16s. 10d. per chaldron,	£42	1	8
25 ,, gas coke, at 10s. 6d. per chaldron, . . .	13	2	6
	<u>£55</u>	<u>4</u>	<u>2</u>

Or the cost per ton equals nearly 8s. 4d. Of course, this includes also the cost of drying the slip over the coke ovens.

Gibbons' Patent Chambers.—In a plan of drying patented by Mr. R. A. Gibbons, which is shown in the accompanying illustration (Fig. 33), the hot gases from the kiln pass both under and over the substances to be dried, and by this means it is claimed that a larger amount of heating surface is obtained, and the sublimed sulphur compounds are less liable to be deposited on the top of the slurry. Two or more chambers are employed, which are used alternately, the heat passing both under and over the material to be dried.

Michele's Chambers.—In a somewhat similar way Mr. V. de Michele uses the exterior surfaces of the arches, as well as the floor of the chambers, for drying the slurry. For this purpose the arches are very lightly constructed, and, as will be seen from our illustration (Fig. 34), which gives a section through a series of chambers, they have a roof above them to protect them from the weather, so that an additional quantity of the raw material may be dried on the top of the chambers. It is necessary, however, to spread the slurry on these arched surfaces by hand, and this must, we think, entail a considerable amount of labour.

The Batchelor Kiln.—This is shown in Fig. 35. At the back of the burning portion two or three arched chambers are arranged, one above the other. The products of combustion pass into and circulate through the chambers, and are finally discharged into a chimney at the rear end of the kiln, one powerful chimney frequently serving for a block or group of kilns. The slurry is contained in the spaces between the arches covering the uppermost chamber, from which it is admitted to the floors by passages. This kiln may be lit as soon as it is charged, the covering of the floors going on during the early stage of burning when little heat is passing off.

Drying Chambers for Raw Material in the form of Bricks.—When the cement compound is made into bricks or blocks, the drying chambers attached to the kilns on the plan arranged by ourselves, and shown in the illustration (Fig. 36), may be used with considerable advan-

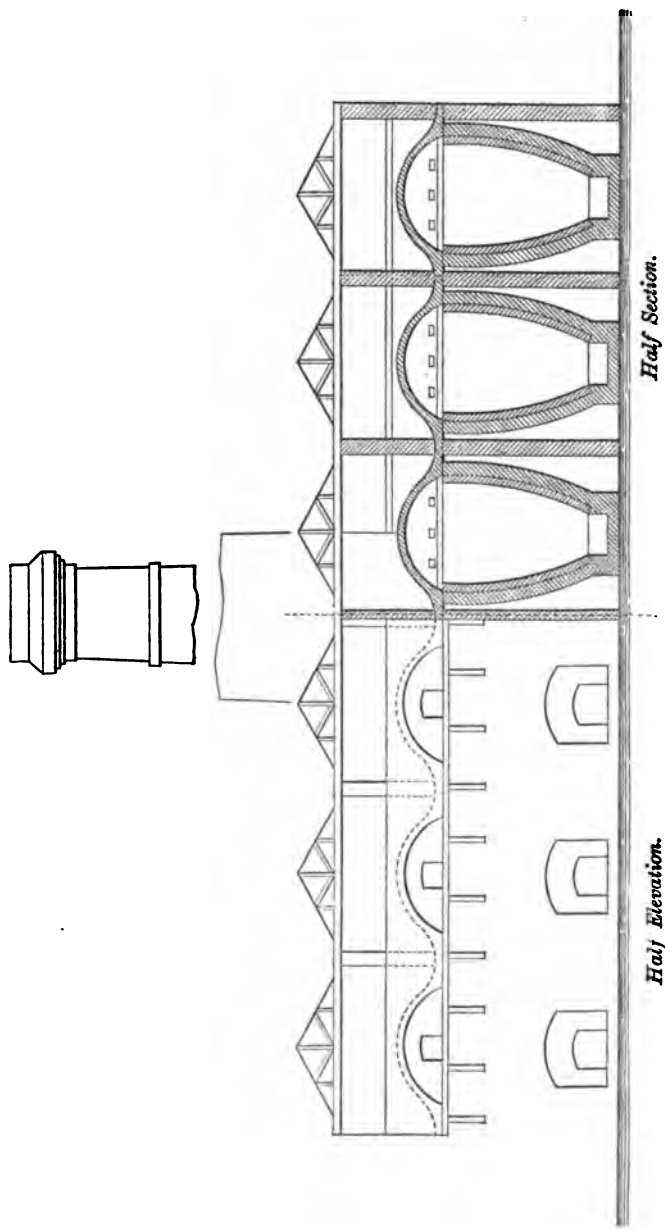
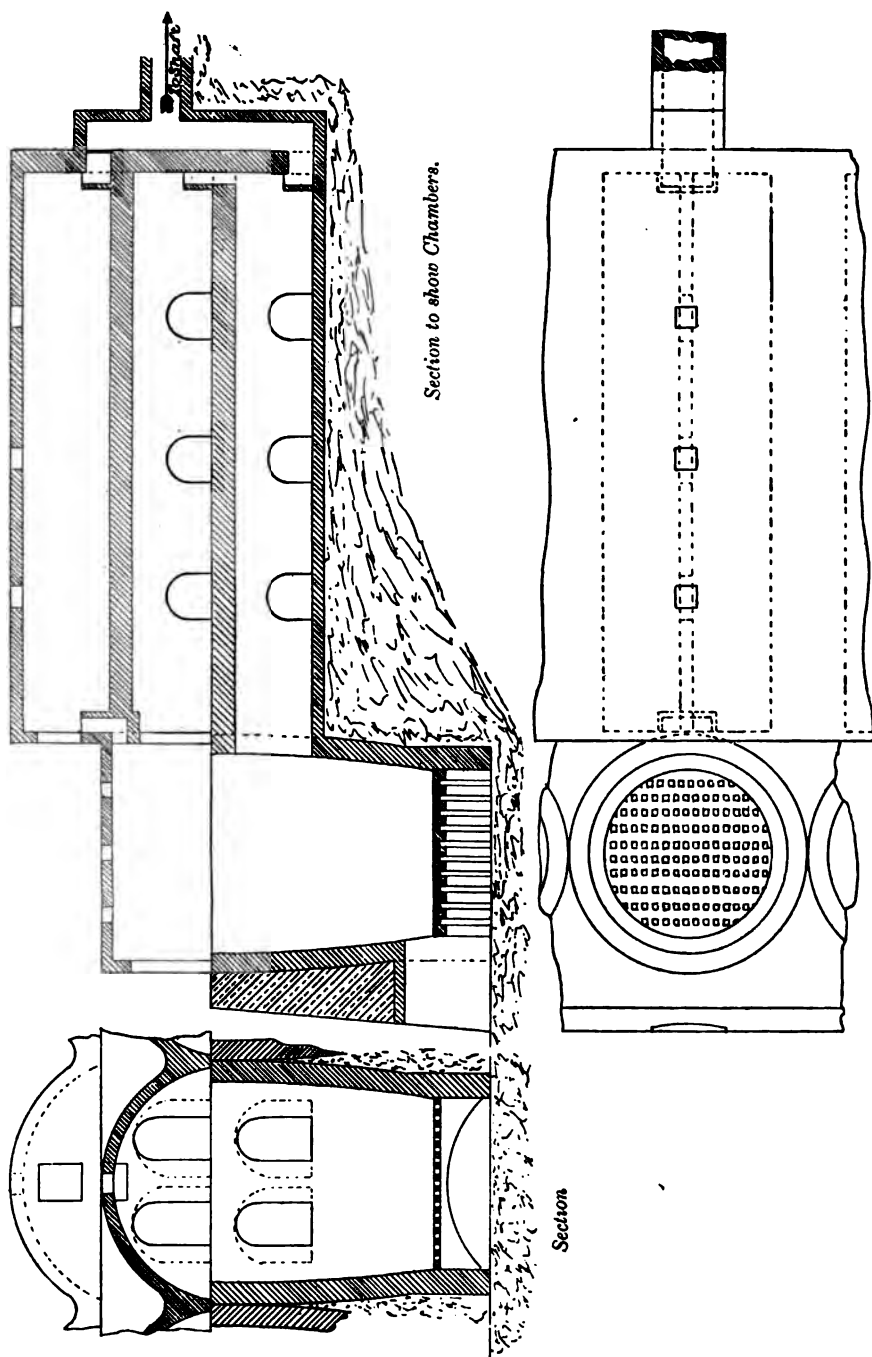


Fig. 34.—Michelet's Patent Chambers.



Plan.
Fig. 35.—The Batchelor Kiln, with Drying Chambers.

tage. It will be seen that, in this invention, the chambers are rectangular in form, and are placed alongside the kilns at such a level as to be most

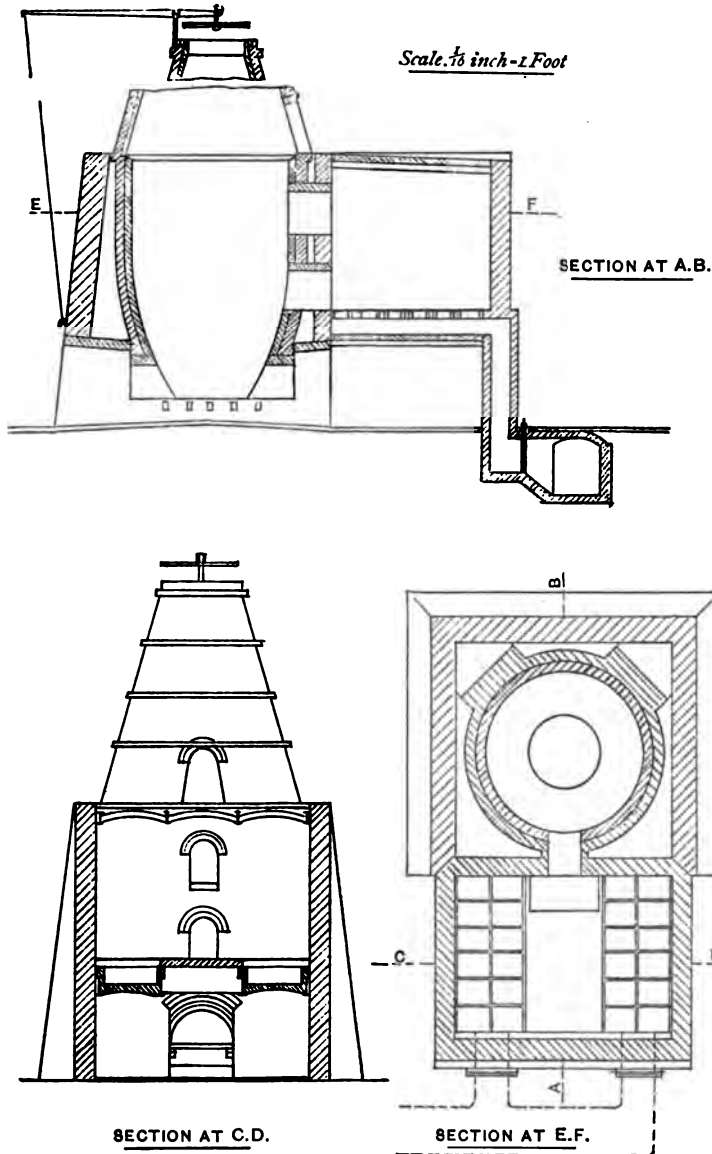


Fig. 36.—Spackman's Drying Chambers.

convenient for the loading operations. The kilns, which are of the usual type, with a conical chimney, are burnt in the ordinary way with inter-

stratified fuel. The orifice of the cone is provided with a damper, and when the charge is in full fire and the combustion is nearly completed, the upper damper is closed, and the dampers in connection with the underground flues leading to a lofty chimney are raised. By this means the hot gases from the kiln are drawn through the chamber, passing downwards in special flues, constructed in the contents, to orifices in the floors of the drying chamber, which will be seen in the section at A B. The heat of the kiln in cooling is found in practice to be amply sufficient to dry the contents of the chamber, which may conveniently be semi-dry bricks produced by means of any of the machines at present employed for the manufacture of bricks of this kind. The size of the chamber is calculated to furnish a full charge for the kiln, and there are suitable openings both for filling the chamber and for loading the kiln. It will be expedient in arranging for the use of chambers of this kind, which are very economical in working, to place the brick machines at such a level that the bricks, as soon as they are pressed, can be wheeled into the chamber, and stacked in position.

The Gases evolved from Cement Kilns.—In certain localities where cement works have been established in the midst of a residential population, and where kilns are used of the type previously employed, the fumes evolved during the process of burning the cement, and the smoke from the drying floors and chimneys, have caused more or less nuisance, and have been objected to by the inhabitants. It may, therefore, be as well to consider briefly the grounds for these complaints, and to show how these evils may best be avoided or mitigated. In this enquiry we cannot do better than avail ourselves largely of the able report by Mr. A. Blaikie on "Cement Works in Kent," which will be found in the *Twentieth Annual Report on Alkali, &c., Works for the Year 1883*. The inspector states that "for the purpose of ascertaining the character of the kiln gases emitted, and of tracing any changes that might take place in them from day to day as the kiln burnt out, a number of analyses were made of washings of gases taken both from the tops of open kilns and from the flues or chambers of close kilns." He points out that "the usual time required for burning out a large kiln is from three to four days. On the first day a white vapour is given off, which consists practically of nothing but moisture, almost no solid matter or smell being present. It is, however, in some states of the weather, very dense. On the second day, as the heat gets up, the smell is often rank and offensive; a smell of burning organic matter is given off by the slip, and there is also some smell from the coke. This vapour is white and very heavy; it contains a quantity of solid matter, and is usually slightly alkaline, as the gases from the fire passing through the upper layers of dried slip are

neutralised and carry away fine particles of chalk. On the third day, sometimes not till the fourth, the kiln is at its greatest heat and beginning to burn out, the vapour being very much lighter and less dense. It has much less smell than the vapour on the second day, but contains much more volatile matter, chiefly chlorides and sulphates of the alkalies, and it has been found that the quantity of chlorides in the washings always increases with the increase of solid matter. The sodium chloride is derived from the water used in preparing the slip, which, as a rule, is very salt, and the potassium is probably liberated from the clay (which contains about 0.6 per cent.) by the action of the chalk. During the later stages the amount of the carbonic oxide is large, and to those close by, and inhaling it, poisonous. The gases are also slightly (in most cases very slightly) acid." Mr. Blaikie shows that the nuisance is generally more acute in the case of the common open kilns than in those which are provided with a chamber on the Johnson system, or which discharge their gases into flues for drying the slurry on various principles which he describes—the plans of Messrs. Burge, White & Glover, and Margetts. In all these latter kilns there must of necessity be a lofty chimney, which causes the gases to be diluted and dispersed. He traces no evil effects on vegetation arising from the fumes caused by cement works, but he says:—"Near one works, some years ago, there was a fine group of elm trees, and these have all been killed since the coke ovens were erected." He notices, on the other hand, the beneficial effects of these works in causing the disappearance of ague, though we think it is more than doubtful whether there is any connection between the manufacture of cement and the gradual decrease in the prevalence of this disorder. It is often stated that the vapours and fumes evolved from lime kilns have a good effect upon phthisic and consumptive patients, but we have never seen any statistics which can be quoted in support of either of these allegations.

Shaft Kilns.—The kilns previously considered have been entirely of the intermittent type, the products of combustion from the open kilns being wasted, those from chamber kilns being employed to dry the slurry for the succeeding charge. The consumption of coke is about the same in both cases, but it is occasionally higher in close than in open kilns, this being due to restricted draught. At an early period of the Portland cement industry, attempts were made to burn the open kiln continuously, clinker being drawn from the bottom at intervals, while, as the charge consequently lowered, dry slurry and coke were added at the top. Thus the waste gases assisted in the calcination of the dry slurry, which was thrown on as soon as the fire showed signs of coming through the uppermost layers of the contents; the proportion of coke to slurry being considerably less than if the kiln was burned intermittently. Although a saving of fuel was effected by this method, it met with only partial

success. The shape of the kiln, broad and low and contracted at its lower portion, was unsuitable. If, as was often the case, the clinker melted to the walls of the kiln and hung up or bridged, it was generally found necessary to allow it to cool down, and to empty and re-start the kiln. These difficulties would without doubt have been at that time surmounted, but, with the introduction of chamber kilns, continuous burning offered no inducement to manufacturers by the wet process. As a set-off to the saving of fuel in the kiln, the slurry had to be dried independently of it, and in the face of the expense of the fuel for this process, and for the labour required for handling, it was found less costly to burn the extra fuel in the kilns and to move the slurry by pumping. The high and increasing cost of gas coke, and the introduction of improved methods of drying, have during recent years caused a considerable amount of attention, principally by foreign inventors, to the construction of vertical continuous kilns, which, from their comparatively small diameter combined with great height, are frequently called shaft kilns. They are employed to a considerable extent on the Continent and in many other parts of the world. For the dry process they are without doubt the best form of fixed kiln that can be used, especially if semi-dry bricks are made from the raw material. In many cases such bricks may go direct from the machine to the kiln, while, if the type of kiln does not admit of the use of damp bricks, the cost of drying them is small. For the wet process, the cost of labour for drying and handling the slurry must always be a drawback to their use in this country. Any kilns of this type will work best if the raw material is moulded into the form of bricks or blocks. Some of the most important will now be described.

The Dietzsch Kiln.—The value of this form of kiln for burning Portland cement has been amply demonstrated, and with careful management it has been proved to be very economical in fuel. The kiln may be described as consisting of four sections:—First, at the base is a cooling chamber for the reception of the clinker after it has been calcined in the firing chamber, which forms the second section or middle zone of the kiln. Above this chamber is a level hearth where the fuel is mixed with the raw material, constituting the third section, and above this hearth is the smoking or heating chamber where the supply of raw material is being gradually heated by the waste gases from the firing. This is the fourth section of the kiln. The arrangement will be understood from the diagram (Fig. 37), which illustrates two kilns, built back to back; one being shown in section, the other in elevation. Here A is the smoking or pre-heating chamber, into which the raw cement mixture is charged through the doors situated at E. As all the waste heat of the kiln passes through this chamber to reach the chimney above it, the material becomes heated

to redness before reaching the hearth B. The fuel—small coal of good quality—is introduced through the furnace doors, F, and the material from B is transferred to the calcining portion C. The calcined material,

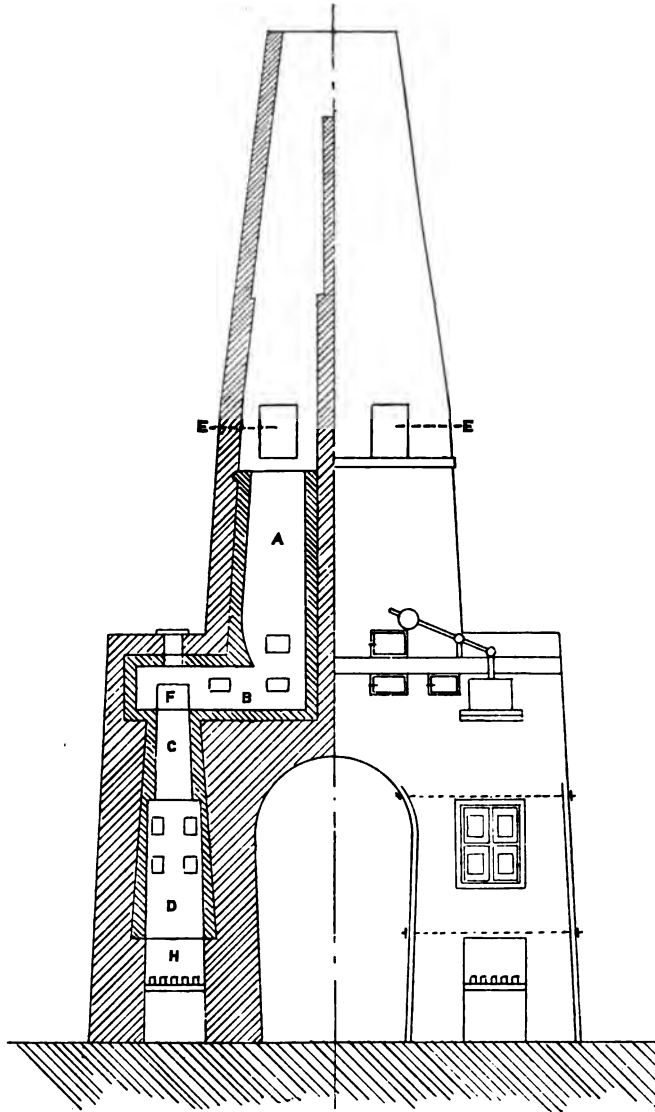


Fig. 37.—The Dietzsch Kiln.

often after having given up the greater part of its heat in D to the air which enters beneath, is drawn out at regular intervals at the bars or

openings, H, and the operation of charging is repeated as the contents of C sink. It is claimed that in this kiln 3 cwts. of small bituminous

or coking coal will burn 1 ton of cement, and, if well managed, there should be no visible smoke. According to the size, the output from a double kiln may vary from 20 to 30 tons in the twenty-four hours.

The Aalborg Kiln, patented by Messrs. F. L. Smidth & Co., of Copenhagen, is a shaft kiln in which the clinkering zone is greatly contracted. It consists therefore of an upper heating chamber of the full width of the shaft, a central combustion chamber of reduced diameter, and below this a cooling chamber, which is again widened out to the full diameter of the shaft. This lower chamber is slightly conical in section with the larger diameter downwards, so as to facilitate the removal of the clinker. The constructive details have been carefully considered, thus the conical chimney is carried on the outer wall of the kiln, and the fire-brick lining is built quite independently, so as to enable the latter to be renewed from time to time when necessary for repairs. As will be seen from the section, Fig. 38, the openings for the introduction of the fuel are placed at intervals round the kiln, and slant downwards so as to deliver the coal below the clinkering zone. The firing holes, when not in use, are closed with iron covers. In this kiln Portland cement is successfully burnt with coal alone, and it is stated that the

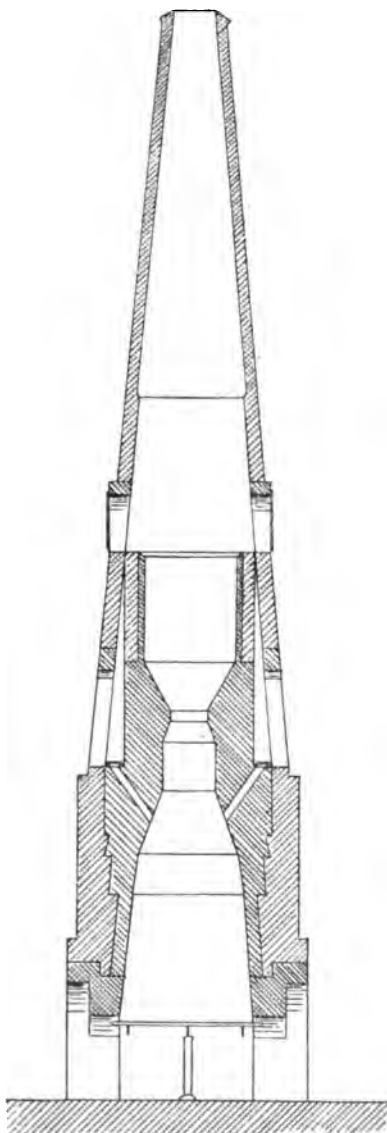


Fig. 38.—The Aalborg Kiln.

weight of the coal needed is but from 12 to 15 per cent. of the weight of the finished cement. In a kiln of this description, which will

yield 100 tons of clinker weekly, the staff of workmen necessary is extremely small, and the fuel consumption, in view of the fact that coal takes the place of coke, is very moderate. The firebrick lining will need to be renewed every alternate year. The clinker, when it has cooled down in the lower chamber, is removed by dropping the firebars in the ordinary way.

The Schneider Kiln.—This kiln has recently attracted much attention in this country. The upper heating chamber is fairly capacious, but the hot zone is relatively small and it should not extend over more than 5 or 6 feet of the total height. Great care is taken to protect the firebrick lining by the use of a specially-contrived filling ring, which enables the burner to surround the raw material with a protective belt of finely-broken slurry or raw flour, about 2 inches in thickness. The fuel used is coke, and the kiln is fed with small quantities at frequent intervals. This kiln is both easy to work and very economical in fuel. A large number of such kilns have been erected on the Continent. The yield of clinker may vary from 10 to 12 tons per day, and the coke required will run from 28 to 38 cwts. for this quantity. The Schneider kiln is not a very expensive one to build, and the cost of repairs is relatively trifling. It is in use in this country for burning cement bricks made by the semi-dry process, which may be put into the kilns direct from the machines, and in some works which use the wet process such kilns are employed for burning surplus slurry from the chambers of the close kilns.

The Hauenschild Kiln.—This kiln, which has undergone many modifications since it was first introduced, consists in its more recent development of a cylindrical shaft which is not sensibly contracted except just above the hot zone, where there is a slight upward contraction towards the upper heating chamber. At the base of the shaft is a firegrate of special construction which is accessible from all the four quarters of the kiln, and the top of the shaft is fitted with a damper or close-fitting cover which can be removed at will and affords the means of inspecting the progress of the calcination process. In the first design the kiln was provided with a cone or hood, in which were four charging doors for loading purposes. In modern practice a horizontal flue in the heating chamber leads into a central chimney which will serve for a group of kilns placed round it. In order to avoid inequalities in the draught, the inventor specifies the use of air under pressure. The mixed coke and slurry, the latter being moulded into hollow prisms, are fed in at intervals at the top by lifting the covers. It is stated that the fuel required for this kiln will be from 16·5 to 18 per cent. of the weight of the calcined clinker. The moulded slurry and the use of powdered lime round the walls of the kiln is said to prevent the adhesion of the clinker to the firebrick.

The Hotop Kiln.—This kiln very closely resembles that invented by Hauenschild. It is circular in plan and may be from 40 to 45 feet in

height. The top is arched over, but it contains an opening in the centre for the escape of the gases, which pass out thence into the chimney, either built above each kiln, or arranged, as in the case of Hauenschild's patent, to serve for a group of kilns. At the base of the kiln is a basket-shaped fire-grate, contracted into a central cylindrical ring through which the clinker can be withdrawn. This arrangement prevents the bridging of the clinker, which frequently causes trouble when the draw-holes are situated at the sides, and which sometimes so far prevents the proper descent of the kiln-contents that the kiln has to be cooled down and emptied. It is always found that the centre of the kiln is the hottest part, and this plan of withdrawing the clinker constitutes an important improvement. In all other respects the management and working of the kiln is identical with that of the shaft kilns previously described. The general arrangement will be understood by reference to the diagram (Fig. 39). The dried bricks or slurry, together with the requisite amount of coke, are fed in at the side through openings provided for the purpose, and the burnt clinker is removed through the centre of the fire-grate. The time required for the charge to pass through the kiln is, under ordinary conditions, about thirty-six hours. Six tons of burnt clinker need 1 ton of coke and the yield is from

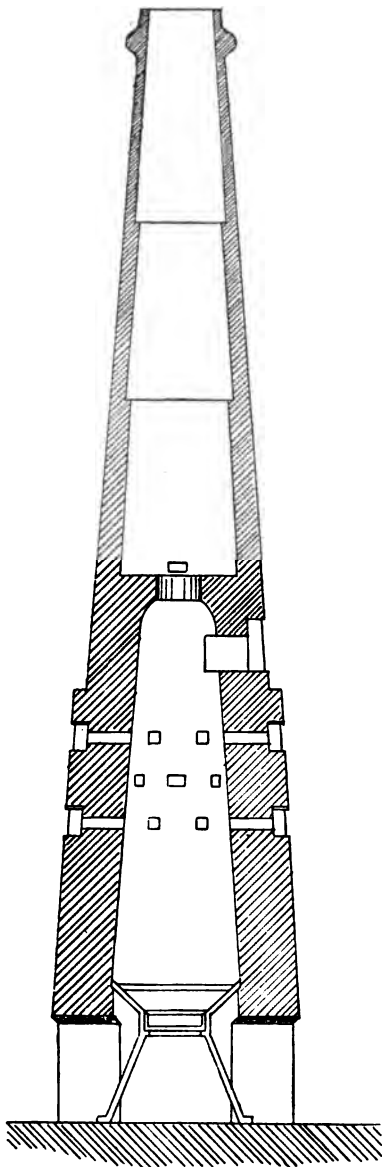


Fig. 39.—The Hotop Kiln—
Sectional View.

12 to 14 tons per diem. A special feature of the kiln is the contrivance for preventing the adhesion of the semi-fused clinker to the firebrick lining. Just above the hot zone is a ring of perforated firebricks with small openings through which iron nozzles project into the kiln. These nozzles are supplied with water, under pressure, from a pipe, which surrounds the kiln, and by this means a stream of cold water can be turned on at any time and can be used to cool down the lining. Another advantage of this arrangement is that the steam which is thus produced renders the outer part of the clinker adjoining the wall of the kiln more friable and porous and thus facilitates the emptying process.

The Stein Ribbed Kiln.—This kiln differs from the other shaft kilns which we have previously described, in that it consists entirely of iron, built up in a series of rings. The cast-iron blocks which compose the rings are provided with ribs or webs on the exterior, and these are used with a threefold object—first, in order to strengthen the shaft; second, to prevent the distortion likely to arise in the hot zone, owing to the great heat; and third, to avoid the clinging of the kiln contents to the lining, in consequence of the partial fusion of the clinker. The shaft, or kiln proper, rests on four piers of masonry which are united in pairs by means of cross walls to half their height. These piers are further stiffened and tied together by joists, angle irons, and cross ties. Above them is the iron bed-plate which serves as the foundation of the shaft, and on this is erected the superstructure consisting of cast-iron curved rings, which are each kept in place by a small projecting fillet on the inner edge and these segments key one into the other. They are maintained in position also by their own weight, which is very considerable, and the joints are rendered tight by a coating of slurry. The rings are each 1 foot 8 inches in height, and the diameter of the kiln is made either 6 feet 7 inches or 8 feet 2 inches. The height of the former kiln being 23 feet and of the latter 29 feet 6 inches. Above the uppermost ring is a conical hood formed of stout sheet iron, and this is provided with three or four feeding-holes, fitted with doors or shutters. Above the hood is the chimney, which is likewise formed of sheet iron, and which must equal in height the body of the kiln. The chimney should have a diameter varying from 2 feet 3 inches to 3 feet 3 inches, in accordance with the size of the kiln. The top of the chimney is fitted with a damper in order to regulate the draught. In its action this kiln is, of course, continuous, and it is claimed for it that it entirely prevents all tendency in the clinker to adhere to the sides or walls, and that it can be worked with extraordinary regularity. It has been stated that a kiln of this kind has been run for nine months continuously without interruption of any kind.

The yield of a kiln, 8 feet 2 inches in diameter, fed with half bricks which burn more readily than whole ones, is stated to be 16 tons per diem.

A special form of basket-grate has been designed, also, for this kiln which renders the operation of drawing extremely simple. Though the iron kilns are said to have given such excellent results abroad, some kilns on this principle, which have come under the authors' observation have not proved altogether successful, and it is evident that great care and skill are needed to burn them with satisfactory results.

The Hoffmann Kiln, which was originally introduced for the burning of bricks, has been employed, chiefly on the Continent, with complete success, for the production of Portland cement clinker. In this country, although it has, as already stated, been from time to time used by Portland cement manufacturers, and has been subjected to lengthy trial, it has, so far as we know, never achieved satisfactory results. It consists of an arched tunnel-shaped firing chamber, which may be circular or oval on plan, or may consist of two parallel tunnels joined by means of semi-circular ends, so as to produce an endless kiln, capable of being subdivided into a series of compartments of nearly equal size by means of cross partitions of a temporary character, which may consist of removable iron screens. From each of these divisions or cells, flues are formed to a central smoke chamber surrounding the lofty chimney. These flues are all of them furnished with dampers, which can be closed wholly or partly in order to regulate the draught. The cells have each an external opening in the outer wall of the kiln for loading and unloading, and for the introduction of the above metal screens or partitions. In lieu of wrought iron, it has been for some time past customary to form these screens of paper, as they are fixed in the cool part of the kiln, and serve their purpose for turning the draught until the heat reaches them. Each cell of the kiln is the space enclosed between two such temporary partitions, and the complete kiln may thus consist of from 12 to 20 chambers. When a chamber has been filled with the damp pressed bricks or blocks of slurry, the doorway in the outer wall is carefully built up and plastered over with loam or slurry to render it air-tight. In kilns of this description, employed for burning cement, each of the chambers is bounded by an arched division, the crown of which is considerably below the top of the arch of the kiln. This mode of construction is essential because of the great amount of contraction which takes place in the cement bricks during the progress of firing. These arches tend, therefore, to drive the flames downwards and towards the centre of the tunnel, in lieu of passing along above the contents of the kiln, in the vacant space caused just below the crown of the tunnel in consequence of the sinkage in the clinker.

As an additional safeguard, it is found advisable in Portland cement.

kilns to contrive openings in the crown of the tunnel, adjacent to each of these dividing arches, so that an additional charge of bricks or blocks, mingled with fuel, can be thrown in during the progress of the firing, in order to compensate for this sinking, and to bring the kiln charge right up to the top of the tunnel. In a well-managed kiln it becomes possible by this means to increase the output some 15 per cent. at the cost of a comparatively small increased quantity of fuel. This kiln is illustrated in Fig. 40. Some manufacturers use two cross-arches in each chamber. In burning Portland cement, it is necessary to employ a very powerful draught, and experience has shown that two exits to the chimney should be provided, both on the inner and outer side of each of the chambers, as will be seen in the section at X X.

The bricks are so placed in the chambers as to form continuous flues for the passage of the fire through the mass, and numerous openings in the crown of the kiln seen at Y Y serve for the introduction of the fuel, which is small coal or breeze mixed with coal. The fire passes round and round the kiln in the direction of the draught, and great care and attention must be paid to the feeding of fuel and the management of the dampers, by means of which the draught is regulated. Some manufacturers have been successful in using the Hoffmann kiln with coal alone; indeed it is stated that a kiln at Marseilles is fired with brown coal. Under each of the openings in the vault of the tunnel, it is needful that vertical shafts should lead down to the channels left in the bricks for the passage of the products of combustion, and, as the contents of the kiln shrink together in the progress of the firing, there is a great risk of the collapse of these shafts, or else of the horizontal flues beneath. It is as well to make use of fairly dry bricks or blocks in loading these kilns, and therefore it is usual to subject these bricks to a preliminary drying process; but it is quite possible, with care, to wheel the bricks from the semi-dry presses at once to the chambers, in which state they contain as much as 10 per cent. of water. The heat given out by the clinker in cooling is used to dry and warm up the green bricks, and owing to the very complete utilisation of the products of combustion, it will readily be understood that this system of burning is a very economical one. Kilns of this type were used more than forty years ago by Messrs. Dyckerhoff & Sons on the Rhine, near Biebrich, and the firm still employ six Hoffmann kilns, with an output of about 100,000 tons of cement annually. At the present time the annular kilns are used at a large number of cement works in Germany, Austria, France, Switzerland, and even in Japan and the Transvaal. The average yield per kiln amounts to about 16,000 tons per annum, but the output depends very largely upon the skill of the burner, and the speed with which the fire is driven round. It is usual to work at the rate of filling one chamber every day, which implies, of course, the emptying of a second chamber.

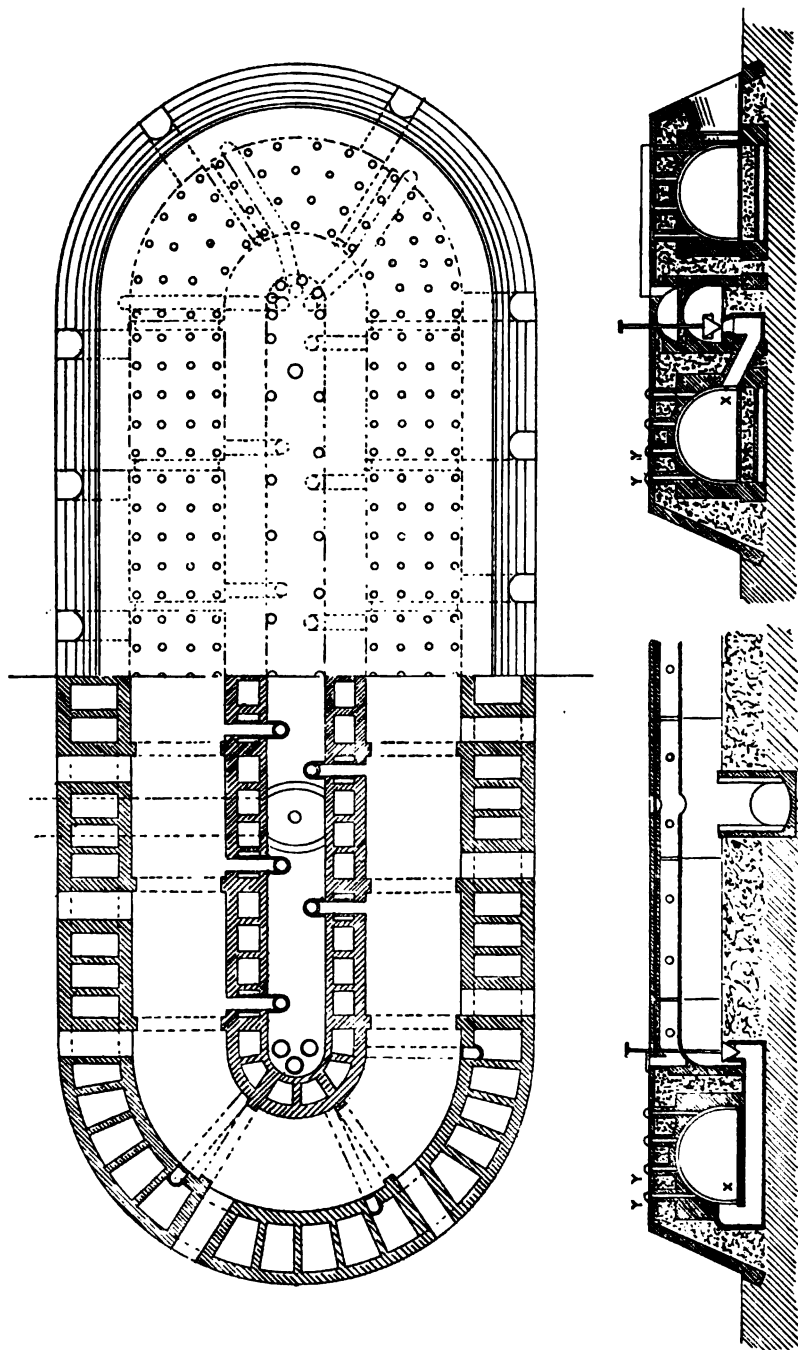


Fig. 40.—The Hoffmann Kiln—Plan and Sections.

CHAPTER XII.

THE CALCINATION OF THE CEMENT MIXTURE—REVOLVING OR ROTARY KILNS.

CONTENTS.—The Rotary System of Crampton—Ransome's Rotary Kiln—Stokes' Rotary Kiln—Rotary Kiln in America—Ransome's American Patent—The Hurry & Seaman Rotary Kiln—Newberry's use of Rotary Kiln for Wet Process—Regenerating Process—The Modern Rotary Kiln—The Lining of Rotary Kilns—Fuel in Rotary Kilns—Coal Grinding—Clinker Cooling Systems—Clinker Coolers—Shaking Coolers—Fuel Consumption and Output.

The Rotary System of Crampton.—The proposal to employ a revolving furnace for the calcination of Portland cement originated in this country with Mr. T. R. Crampton, who obtained a patent for his process in 1877. The furnace was fired by powdered fuel injected by compressed air, but it does not seem to have been commercially employed, although at this time revolving furnaces were in use in the alkali manufacture, and had been patented by Siemens in 1869.

Ransome's Rotary Kiln.—In May, 1885, Mr. Frederick Ransome patented a rotary kiln for burning cement, which achieved some measure of success, and which was undoubtedly the forerunner of the modern improved system of burning in revolving kilns. The Ransome kiln consisted of an inclined cylindrical furnace, about 25 feet in length, which was carried on roller bearings, and was caused to rotate by means of worm-gearing. The firebrick lining had a series of projecting courses, so arranged as to form longitudinal ridges. The powdered raw material was fed in by means of a hopper at the upper end, and travelled slowly down the furnace, being turned over and over by the constant revolutions of the kiln, moreover it was caught up and made to fall across the cylinder by the presence of these internal projections. The firing was effected by means of producer-gas, which entered the kiln at the opposite end, and produced large volumes of flame. The cement materials, as they passed forward, were gradually heated to the clinkering stage, and ultimately fell into a pit situated beneath the lowest part of the cylinder. The inventor proposed to burn the cement in the form of a fine powder, and by this means to dispense with the subsequent grinding. His aim was not alone to secure economy in the use of fuel, but he also hoped by preliminary grinding and sifting of the powdered slurry to turn out a finished Portland cement. He

entirely failed to grasp the fact that, in order to produce a suitable clinker, it was necessary to reach the stage of incipient fusion, and, in its passage through the kiln, the finely-ground cement materials caked together and adhered in a sticky mass to the linings. This caking of the clinker proved the ruin of the process, though Mr. Ransome had other difficulties to contend with. It was found, also, that the finely-divided cement material was carried by the draught right out of the kiln, and had to be intercepted at the exit-end and returned to the feeding hopper. The use of producer-gas, without a regenerator, failed to yield the requisite steady temperature for the calcination process, and when a regenerator was added, it speedily became clogged with the cement powder, carried away into it by the draught. The cement mixture had to be highly limed, and this resulted in a very quick-setting cement, and, owing to the shortness of the tube, it was impossible to utilise the full heating value of the fuel. The working of the kiln was, moreover, constantly interrupted by the balling of the clinker, which collected into lumps and cakes, and stuck, as we have seen, to the linings of the hot zone of the cylinder. After prolonged trials and many costly failures, the Ransome rotary kilns were abandoned as impracticable by English cement manufacturers.

Stokes' Rotary Kiln.—A greater measure of success was obtained by the invention of Mr. Wilfred Stokes, who profited by certain of the mistakes of the Ransome kiln, and utilised the heat in a more advantageous way. In the Stokes process, a burning cylinder 5 feet in diameter and 35 feet in length was employed; this was formed of steel plates, resting on two sets of friction rollers, set in a cast-iron cradle. This cylinder, which was lined with firebrick, was driven by means of spur gearing, about one revolution per minute, and the waste gas, escaping from the burning cylinder, passed through a second cylinder, 40 feet in length by 12 feet in diameter, set horizontally, and caused to rotate slowly on friction wheels, being driven by worm gearing. The outside of this drum was coated with wet slurry by a dipping arrangement, and the slurry was slowly dried by the hot walls of the drum, to which it adhered. By the time the drum had nearly completed one revolution, the already dried material was scraped off in flakes by a series of chain scrapers, and delivered into the feed-shoot of the burning cylinder. A third cylinder was placed at the lower end of the burning cylinder, and received the red-hot clinker as it issued from the kiln. This cylinder, which was of the same size as the burning cylinder, was provided internally with gills to assist in cooling the clinker as it passed through it, and the current of air driven through the cylinder was used to mix with the producer-gas employed in the burning cylinder.

Although Mr. Stokes encountered many difficulties in working out

his inventions, most of which he was successful in overcoming, he, too, found the attack of the fused clinker upon the kiln-linings a constant drawback to the satisfactory working of the process; and in spite of the introduction of magnesia bricks and bricks made of bauxite, which last proved to be too soft and friable to stand the wear of the kiln, the mechanical defects proved to be insuperable, and the continued use of this form of kiln was rendered impossible.

The Rotary Kiln in America.—The Portland cement industry was established by Mr. D. O. Saylor, at Coplay, in Pennsylvania, about 1876, and during the next few years several other plants of small capacity were erected in various parts of the United States. In all of them European methods of manufacture were followed, but although the product was good, it could not compete, as regards cost, with imported cement. These methods involved a considerable amount of labour, and the high cost of this labour as compared with the wages paid in England, and to a still greater extent with those current in Germany, these being the principal exporting countries, rendered the industry unprofitable. The rotary kiln presented a possible solution of this difficulty, and in the hands of M. Pierre Giron, who was the superintendent of the Atlas Cement Works in Pennsylvania, it proved, after many failures and experiments, a success. About 1893 Mr. S. B. Newberry employed rotary kilns 80 feet in length for burning wet slurry; the fuel employed in both these cases was petroleum oil. In 1895 Messrs. Lathbury and Spackman conducted a series of trials, extending over four months, at the works of the Alpha Company, in the use of pulverised coal, as a substitute for crude oil, which previously had been exclusively employed as fuel in all the rotary kilns in America. About the same time the Atlas Cement Company perfected arrangements for the use of coal dust, and now the employment of this material has almost entirely supplanted the oil at first used. It seems impossible to decide to whom the real merit of the present system of using powdered coal belongs, and the patent was refused in the United States Courts to both the rival applicants.

Ransome's American Patent.—Ransome's American patent dates from 1886, and it was first used in the United States at a cement works on the Hudson River, near Rondout, by the Atlas Portland Cement Company, and later, with more favourable raw material, at Coplay, in the Lehigh Valley of Pennsylvania. The hard dry materials found at Coplay were in every way adapted for use in rotary kilns, and in course of time, and after great outlay upon experiments, the process, as modified by Mr. T. F. Navarro, proved entirely satisfactory.

The Hurry and Seaman Rotary Kiln.—Further improvements in the rotary kiln process were introduced later by Messrs. Hurry and

Seaman, who patented their invention in 1895. The chief advantage derived under their patent was economy in the use of fuel by utilising the heat from the clinker in two auxiliary cylinders. In the first of these cylinders the clinker was received as it fell from the kiln, and a stream of air passing over it became heated and served to ignite the coal dust in the burning cylinder. In a lower cylinder the clinker, which had been crushed and sprinkled with water, was exposed to a further current of air in order to complete the cooling and drying.

Newberry: Use of Rotary Kilns for Wet Process.—While these inventions were being perfected for the dry materials, Mr. Spencer B. Newberry, as we have seen, was carrying on successful experiments at Warners, New York, in the use of rotary kilns for the wet process. He employed a double set of kilns, one being used for drying the wet slurry and the other for the final calcination of the dried material. He afterwards erected a small works at Bay Bridge, near Sandusky, Ohio, and here he again introduced the double system with two 40-foot cylinders. He subsequently riveted the two sections into a single cylinder, 80 feet in length, into which the wet slurry was at once introduced, so as to complete the drying and firing in a single operation; but, after many trials, he concluded that kilns of this great length were not so well adapted for the purpose as shorter ones, and the most recent practice has been to make use of cylinders not exceeding 60 feet in length.

Regenerating Process.—Notwithstanding the efforts at first made to take advantage of the heat of the clinker and of the chimney gases, it is found that very little practical gain can be secured by the various expedients which have from time to time been proposed to effect these economies, and in the present use of rotary kilns, with the exception of the occasional employment of the heat, given up by the clinker in cooling, for raising the temperature of the injected air, these sources of heat are disregarded.

The Modern Rotary Kiln.—The Ransome rotary kiln was, as we have seen, 25 feet in length, and the difficulty with its use, both in this country and in America, was that of fully calcining the raw material before it was discharged from the cylinder, which was undoubtedly too short. In some of the early experiments in America, with powdered coal as fuel, 30-foot cylinders were used, but the flame traversed their whole length, and much of the heat was consequently lost. The length was increased to 50 and then to 60 feet with better results. Although cylinders extending up to 90 feet are in some cases employed, the usual length is now 60 or 70 feet, with a uniform diameter of 6 feet. The Hurry and Seaman kilns are made 6 feet 6 inches in diameter at the lower or discharge end, reducing to 5 feet 6 inches in diameter at the upper end. This is the usual practice with kilns of greater diameter than

6 feet, but the great majority of rotary kilns are now made with a continuous diameter of 6 feet. The cylinders are constructed of steel plates riveted together with butt straps, and they are carried upon rollers upon which they rotate. They are set at a slight inclination, which varies with the raw materials used and with their fusibility. For the slurry of the wet process it has been found that a gradient of $\frac{1}{2}$ inch to the foot gives the best results, while for dry materials an inclination of from $\frac{1}{8}$ to $\frac{1}{4}$ of an inch to the foot is used. The minimum and maximum speed of rotation depends upon the incline of the kiln and on the nature of the

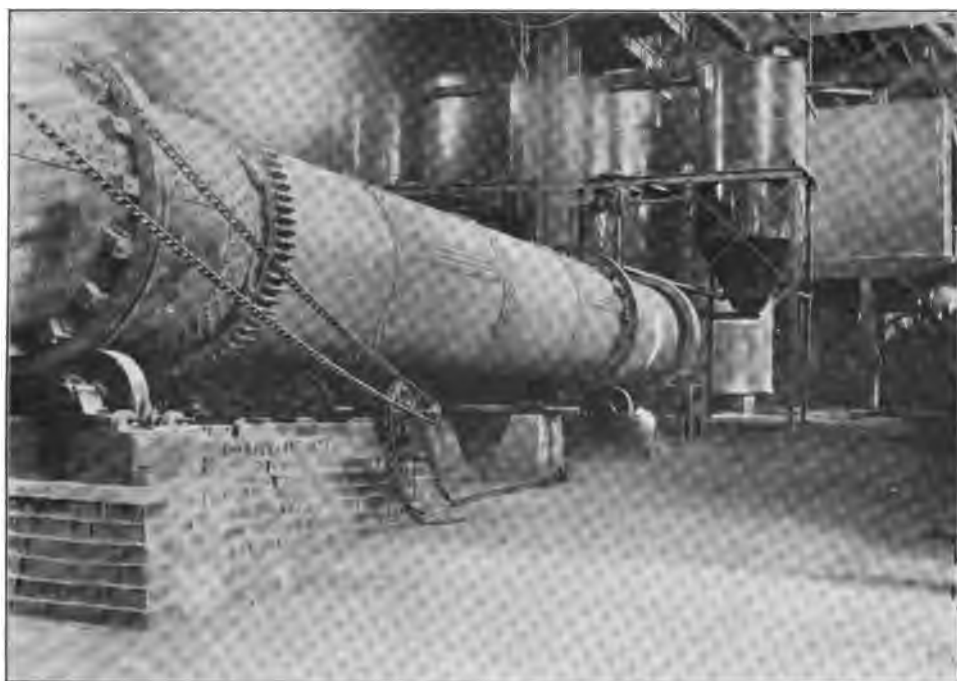


Fig. 41.—Lathbury-Spackman Rotary Kiln—General View.

raw material under treatment. It may also vary in accordance with the conditions of heat in the kiln, but the average minimum speed is about 20 turns in the hour, and the average maximum rate of drive is about 60 revolutions in the hour. The nature of the materials must, of course, have considerable influence upon the rapidity with which the kiln is driven; the most satisfactory results are obtained by using speed regulators on the driving arrangements, both for kilns and for the coal feeds, thus placing the speeds under the direct control of the burner, with power to alter the same immediately at will.

An iron chimney is provided at the upper end of each kiln. The slurry of the wet process is stored in tanks, and is delivered into the kiln by pumping; the flour of the dry process is fed from bins by a worm-conveyor, working in a water-jacketed case. The fuel now almost universally employed is powdered coal, which is blown in at the lower end either by a fan, by compressed air, or by a jet of high-pressure steam. Means are provided for regulating the air-supply. The finely-divided fuel at once bursts into flame, and the raw material in its downward passage through the kiln is gradually dehydrated and deprived of its carbonic acid. Upon reaching a point situated at a distance of about 15 feet from the end, vitrification commences, and the clinker is finally delivered at a white heat, in sizes varying from a pea to a walnut, from the end of the cylinder, having a temperature of about $1,350^{\circ}\text{C}$.

With dry raw materials the temperature of the chimney gases may range from about 450°C . to 650°C .; with the slurry of the wet process, the average may be from 200° to 300°C .

The Lining of Rotary Kilns.—Perhaps no single detail in the use of rotary kilns has been of greater importance than the question of the kiln lining. It was here, as we have seen, that the earlier inventors in all cases failed, and the ultimate success of this system of calcining became assured when this difficulty had been effectually overcome. The firebrick usually employed for refractory purposes contains a high percentage of silica, and behaves as an acid substance in the presence of the Portland cement clinker, which is a basic material. At a clinkering temperature these substances react, and the linings are rapidly attacked and destroyed. Magnesia bricks were found to crack, shrink, and drop out of their places. The most satisfactory results have been obtained for kilns working both under the dry and wet processes by the use of a firebrick containing about 41 per cent. of silica and 49 per cent. of alumina. Attempts have been made to use a firebrick manufactured from cement clinker. This was ground to pass a quarter-inch mesh sieve, and mixed with cement; but the results were not satisfactory, as the bricks would chip and break away at the joints, finally falling out into the kiln. In starting a kiln, a skilful burner will coat that portion of the firebrick lining where the clinkering takes place with a layer of melted clinker, which protects the lining, and in no way interferes with the burning and with the continuous discharge of the contents.

In the case of slurry plants, it is customary to line the tube with firebrick throughout its entire length, but as the heat at the exit end is not sufficient to buckle the plates, nothing seems to be gained by this practice, and good results have been obtained by using a brick lining for about two-thirds of their lengths in the case of 60-foot kilns.

The Fuel in Rotary Kilns.—We have seen that the producer-gas

at first used in the Ransome and the Stokes kilns gave way in the early American experiments to the use of oil as fuel; this in its turn giving place to the employment of powdered coal. Oil is, however, still in use at a plant in California, while at the works of the Iola Portland Cement Company in Kansas, the fuel for both kilns and power is natural gas.



Fig. 42.—Lathbury-Spackman Rotary Kiln—General View.

Oil fuel has been recently used and we believe abandoned in favour of powdered coal at one of the Thames works using rotary kilns. An analysis of the oil-burned clinker is given in the table in p. 78. Quite recently experiments have again been made at an American works with

gas producers, two kilns being fired with powdered coal and two with producer-gas. The output per kiln, and the weight of fuel used, was about the same in each case, but the producer involved the use of a better class of coal, and this was consequently more expensive, while the cost of labour for attending the producers was greater than that necessary when using powdered coal.

Bituminous coal has been found most suitable, anthracite being more difficult of ignition. The coal must be thoroughly dried before it can be ground, an operation requiring care to avoid loss of volatile constituents. Rotary driers, heated by hot air from the clinker coolers, are generally employed for this purpose. The facility with which the coal is dried depends to some extent upon the constituents of the ash. Coal in which the ash is high in silica dries much more readily and completely than that in which it consists largely of clay.

Coal Grinding.—The coal should be ground so finely as to leave a residue of not more than 4 to 5 per cent. on a test sieve having 10,000 meshes to the square inch. The grinding is usually effected either by Griffin-mills, which recent experience has shown to be especially suitable for the purpose, or by tube-mills. With the latter the preliminary grinding need not be so fine as is necessary in the case of raw flour from hard limestone or cement clinker. The grinding is sometimes done by rollers, by disintegrators, or by ball-mills, these last being smaller in relation to the tube-mills they are set to work with than is necessary when grinding hard materials. Owing to the explosive nature of coal dust, it is necessary that the machinery, whatever it may be, which is employed for grinding, should work free from escaping dust. For the same reason, coal dust cannot be stored after grinding, and it has to be used as ground.

The Aero System.—By what is known as the "Aero System," which is in use to a limited extent in the United States, the coal is ground, without previous drying, in a high-speed centrifugal disintegrator. One machine is fixed in front of the discharge-hood of each kiln, the action of the beaters providing sufficient air, the supply of which can be regulated, for forcing the ground coal direct into the kiln. The disadvantages of the system are that the machine has to be placed very close to the hood of the kiln, which somewhat inconveniences the burner in properly manipulating the kiln. Again, the coal cannot be so finely ground by this type of machine as by those previously mentioned, the result being an increased coal consumption. On the other hand, the cost of drying the coal is saved, while the plant itself is cheaper, being about one-third the cost of rotary drying combined with either Griffin-mill or tube-mill grinding machinery.

Clinker Cooling Systems.—In the early days of the rotary process,

the clinker was allowed to fall from the kilns into heaps which were raked down by hand labour; the hot clinker being cooled by simple exposure to the air. The difficulty of obtaining labour for this work, and its high cost in America, soon led to the introduction of mechanical appliances for cooling the clinker. One of the earliest of these was that of Messrs. Hurry & Seaman, used in connection with their type of kiln. The clinker is discharged from each kiln into a second cylinder, 30 feet long and 3 feet in diameter, lined with firebrick, and revolving about six times as fast as the kiln. Through these cylinders a current of air circulates which abstracts a portion of heat from the clinker, and in its heated state forms the air-supply to the kiln. The cylinders converge in pairs, each pair discharging the now partially-cooled clinker into crushing rolls protected with casing. While passing through the rolls it is sprayed with water, and is discharged into a cylinder 60 feet long by 5 feet in diameter, lined with cast-iron plates, provided with ledges which lift and drop the clinker as it gradually passes through. A current of air circulating through the revolving cylinder completes the cooling process, and also draws off the steam from the rolls. The effect of spraying the clinker with water is to hydrate any uncombined lime present, thus avoiding the necessity of maturing the cement by storing. If properly managed it in no way adversely affects either the grinding of the clinker or the quality of the resulting cement. Various systems of cooling and of obtaining a heated air-supply for the kilns by the use of revolving cylinders are in operation.

Clinker Coolers.—Vertical or tower coolers are sometimes employed the hot clinker as discharged from the kiln being lifted into them by an elevator. They vary considerably in dimensions, in some cases one tower is provided for each kiln, in others one for each pair of kilns. Their internal construction varies, but the principle of their action is much the same in all. The inside of the tower is arranged with conical surfaces, over which the clinker spreads as it travels downwards and is exposed to the action of cold air, supplied through branches from a central blast pipe. Under one of these systems the clinker may also at the same time be sprayed with water.

By the regenerative system of Messrs. Lathbury & Spackman, the clinker is discharged into masonry vaults, situated underneath the discharge-hood of kilns. These vaults have sloping floors, outlets from which open into a tunnel. Cold air is forced into the lower level of the vaults, and, passing through the pile of hot clinker, becomes heated, when it is drawn off and forced back into the kilns, mixed with the pulverised coal. The same system is sometimes carried out above ground in tanks built of steel plate, the clinker being lifted by an elevator.

Shaking Coolers.—Shaking coolers, one being provided for each kiln, have been recently used. These are enclosed inclined trays kept in motion by cams attached to a revolving shaft. The hot clinker falls into them from the discharge-hood of the kilns, it is then, by the jiggling motion, spread over a series of shelves or steps which form the bottom of the tray, and is gradually carried forward and discharged at the lower end. A large area of hot clinker is thus exposed to the action of the air, which is drawn in from both ends and discharged into a hot air chamber. From this chamber the supply of air for the kilns is taken; the remainder passes away by a shaft.

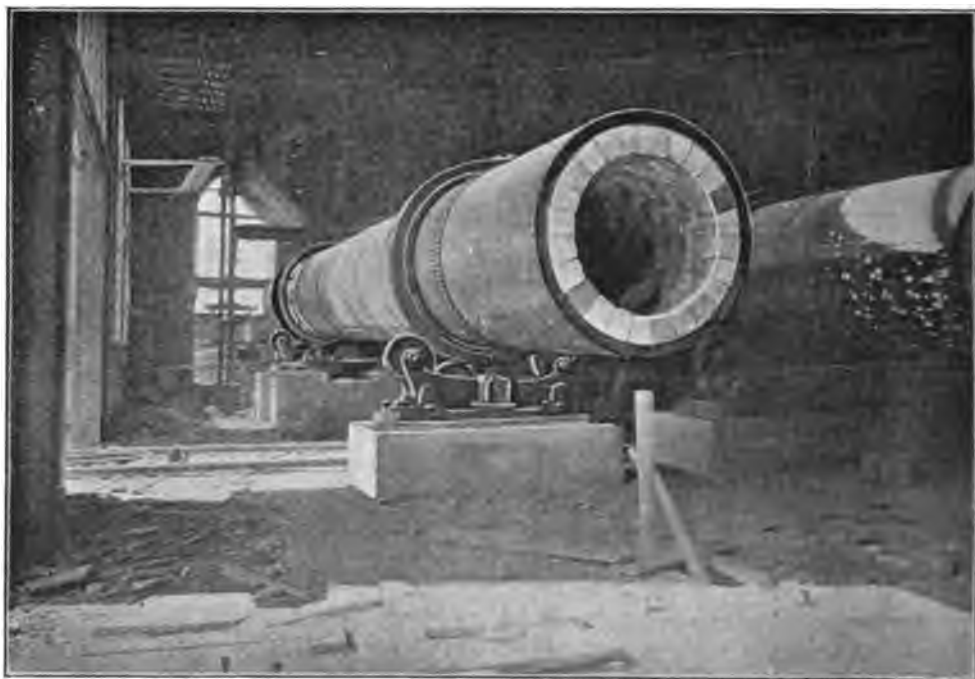


Fig. 43.—Lathbury-Spackman Rotary Kiln—Showing Lining.

Messrs. Lathbury & Spackman of Philadelphia have allowed us to reproduce four illustrations explanatory of their rotary kiln system. Figs. 41 and 42 are general views of one kiln; Fig. 43, kiln fitted with firebrick lining and showing cradles on which the shell is mounted; Fig. 44 indicates in plan and side elevation the disposition of the rotary plant when employed for the wet process and shows the arrangement of two kilns with coal-mill, slurry tanks, and clinker cooler. We have here the most recent and up-to-date appliances for the manufacture of Portland cement, as practised in the United States.

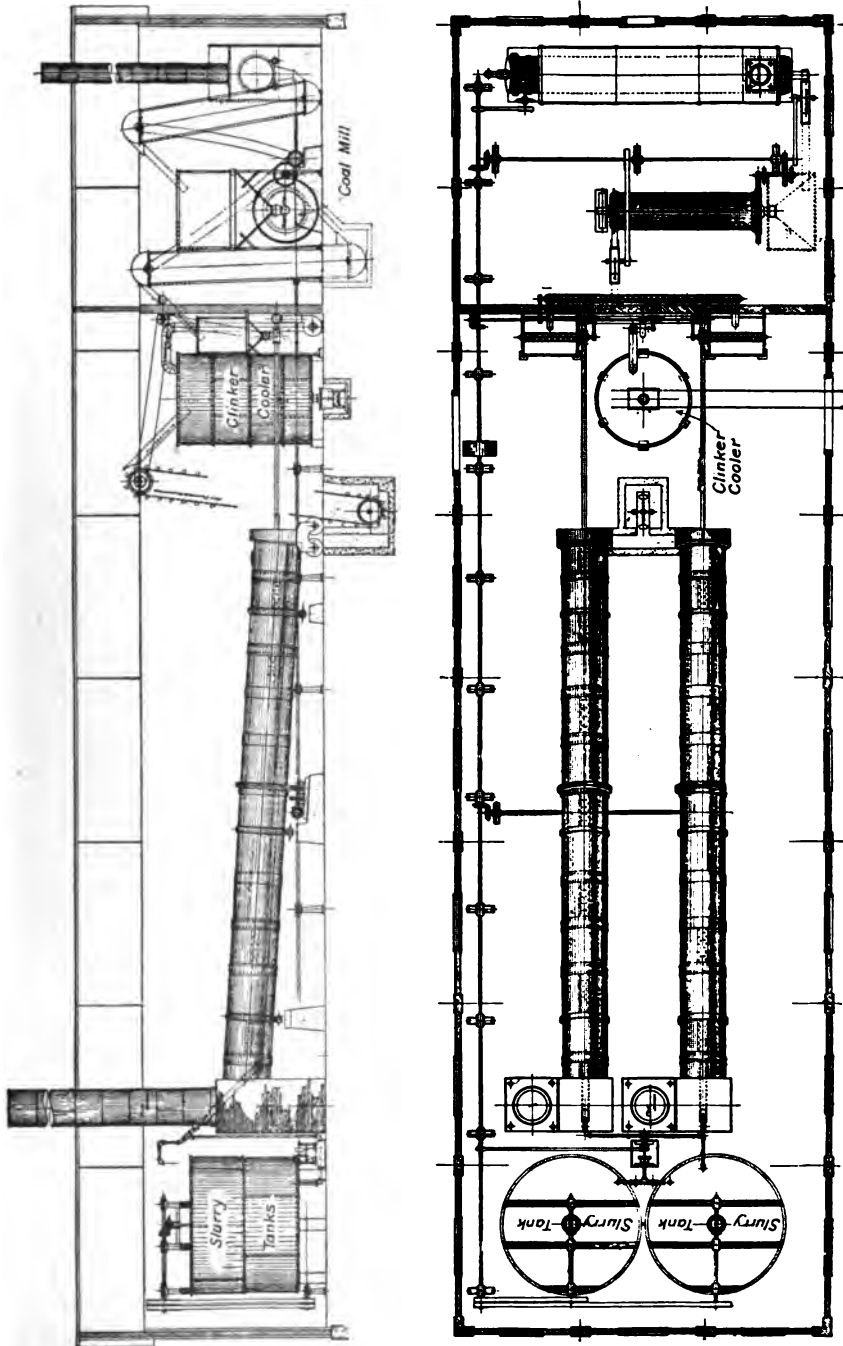


Fig. 44. — Plan and Side Elevation of a Pair of Rotary Kilns.

Fuel Consumption and Output.—Upon these questions very conflicting statements have been made. With slurry, which usually enters the kiln with 50 per cent. of water, the fuel consumption is greater than with dry flour, while the output is less. The production of a rotary kiln is influenced principally by three conditions—the fusibility of the raw materials, the quality of the coal, and the experience of the burner. In recent American practice with dry materials from 650 to 700 lbs. of dry coal are used per ton (2,240 lbs.) of clinker produced, with slurry from 850 to 900 lbs. With slurry the average output per day of twenty-four hours is 21 tons per kiln, with dry flour it may reach 29 tons.

CHAPTER XIII.

**GRINDING, STORING, AND PACKING THE CEMENT—DUST
COLLECTING CONTRIVANCES.**

CONTENTS.—Early Practice—Sifting Machinery—The Air Separator—Difficulties Entailed by Use of Sieves—Rock Emery Millstones—Continental Practice—Roller-mill—Edge-Runner Mill of Dutrulle & Solomons—Neate's Dynamic Grinder—The Freeman Patent Hydraulic Grinder—Recent Practice—Fineness of Grinding—Grinding Tests—Storing and Packing—Dust Collecting Contrivances.

Early Practice.—From the very inception of the Portland cement industry, the method of grinding was for many years almost entirely by the use of French burr millstones; the preliminary crushing being effected either by edge-runner or roller-mills, the latter of various types, the rollers being either plain, corrugated, or provided with teeth. At a later period the use of Blake stonebreakers, or reciprocating-jaw machines of this type, became very general. From the light stones and working parts of the corn-mill, the heavy stones built of hard burrs and the strong massive gearing of the cement-mill were gradually evolved. In the early days, when finely-ground cement was not demanded and when the clinker was not heavily burned, this system of grinding answered very well, the cement being considered finished when it left the mills without any subsequent sifting. With the demand for cement of greater strength, which could only be reached by more highly-limed and more heavily-burned clinker, most difficult to grind, and with the necessity for more finely-ground cement, it was found that this system of grinding left much to be desired.

Degree of Fineness in 1879.—From some notes made in 1879 we give the fineness of ordinary commercial cement of that date. It was ground without sifting from hard well-burned clinker:—

On test-sieve having 30 meshes to the lineal inch 10·0 per cent. of residue.

„	„	40	„	„	25·6	„	„
„	„	50	„	„	31·8	„	„
„	„	100	„	„	44·4	„	„

This cement found a ready market, and as regards fineness it is fairly representative of much of the cement of that time, unless such as was especially ordered to be finely ground and paid for at an increased price. At the present time cement leaving 5 per cent. or even less of residue

on a test-sieve having 100 meshes to the lineal inch is quite an ordinary commercial product.

Sifting Machinery.—About the year 1878 sieves were introduced into some manufactories, but their use at this time was by no means general. Not more than 10 per cent. of residue, on a test-sieve having 50 meshes to the lineal inch, was a condition of many specifications, and this requirement soon became general. Although this fineness could be obtained by careful milling without sifting, it left but little margin, while, as the full weight of the runner had to be kept on the bedstone, when grinding so fine, the wear on the stones and the power absorbed was considerable. There was a danger also of the joints becoming defective, entailing the risk of throwing out coarse fragments. The use of sieves, therefore, extended and became almost universal. A fineness of somewhat less than 10 per cent. of residue on a test-sieve of 50 meshes could be obtained by passing the cement from the mills through a sieve covered with wire cloth having 40 meshes to the inch. The wire cloth or gauze was made of tempered steel wire and the sieves were constructed and arranged in various ways. In some cases several mills were arranged to discharge into a revolving sieve of large capacity, either of circular, hexagonal, or octagonal cross-section, or into a flat shaking sieve. The disadvantage of an arrangement of this kind was that if the sieve got out of order—a by no means uncommon occurrence—all the mills connected with it were stopped. A more usual plan was to provide each mill with its own sieve, generally a flat shaking sieve, with an arrangement to alter the angle at which it was suspended. This regulated the fineness of the cement, for a coarse sieve set at a steep angle will yield as fine a product as a finer one, set so as to be in a position nearly horizontal.

The Air Separator.—About 1884 Messrs. Mumford & Moodie devised and patented a system by which the coarse and fine portions of a roughly-ground material are separated by the action of a current of air. This system was first applied to mills for grinding phosphates, and as introduced and manufactured by Messrs. Askham, it rapidly found its way into the cement industry, and to a considerable extent replaced sieves. Fig. 45 shows a section of the machine, and the following description is that given by the inventors :—

“A, outer casing of sheet iron, circular in form, into which the fine dust is thrown, terminating in a spout at the bottom for delivering into bags, casks, upon creepers, &c., as may be desired. B, inner casing into which the coarse particles fall, and can be delivered to the right or left through the branch pipes, *a, a*, by moving the valve, *c*. C, a movable band encircling the top of the case B, which acts as a damper for closing the opening between the cases A and B, and is worked by the lever, *f*,

and the rods, *h, h*. *D*, hood against which the material is thrown. *E, E*, blades of fan connected by arms to the disc, *E¹*, rotating on the fan spindle, *E²*. *F*, standard for carrying the spindle and driving gear, which may be bevel wheels or pulleys. *G*, feed cone into which the material is fed.

"The material to be treated is fed into the cone, *G*, and, falling upon the rotating disc, *E¹*, it is thrown in a thin stream all round towards the fixed hood, *D*. The current induced by the fan passes upwards and carries with it the fine particles, which are thrown into the outer case *A*; the current of air, separating itself from the fine particles by centrifugal force, returns through the opening in the direction of the arrows, the same air being used over and over again. The coarser particles, which are too heavy to be lifted by the current of air, fall into the casing, *B*, from whence they return by the branch pipes, *a, a*, to the grinding machines to be further reduced.

"The degree of fineness of the finished material can be regulated by the speed of the fan, also by the partial closing of the aperture, and by means of the damper, *C*, which intercepts the current of air.

"Different forms of hood, *D*, also alter the quality of the finished material."

Difficulties entailed by the use of Sieves or Separators.—While a much finer product could be obtained by the use of separators than was possible with sieves, one difficulty was common to both systems—viz., that of dealing with the residue or rejected core. It was not possible to grind finely, leaving the sieves or separators to take out a small percentage of coarse matter; as a fine floury product chokes up the meshes of the sieves, in spite of many ingenious devices for shaking or keeping them vibrated, while separators will not deal with a finely-ground material. It is necessary for their successful working that a considerable proportion of the material treated should be in the form of coarse grains, from which the

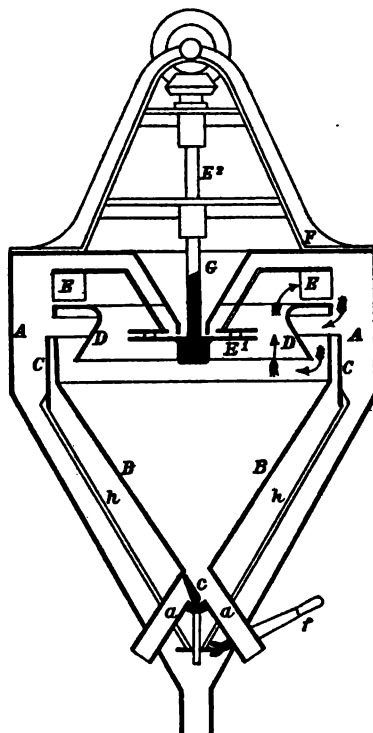


Fig. 45.—The Mumford & Moodie Air Separator.

fine powder may be blown away. On the other hand, if the grinding was too coarse, the resulting cement was not only granular and wanting in impalpable powder, but a much larger proportion of core or coarse residue required re-grinding. The re-grinding of this separated core, consisting as it did of the hardest portions of the clinker, was always troublesome. With French burr-mills it was impossible to grind it alone, as it simply rushed through the stones like water, coming away in much the same condition as it entered.

The only possible method of dealing with it was by mixing it with fresh clinker, and even then much of it passed through unground, to be again rejected and returned. In the state as rejected from the sieves or separators, it was usual to return it to the storage hoppers over the grinding mills, to be mixed with the fresh clinker. We have written of this system of grinding as a thing of the past, for although French burr millstones are still to some extent employed, as will be explained later, their use for fine grinding, as has been described, has practically ceased. Air separators are, however, still in use, and will be referred to subsequently.

Rock-Emery Millstones.—Millstones of French burr require re-dressing after from 30 to 40 hours' use on good clinker. The output begins to diminish long before they are thrown out of work for this purpose, and for the last few hours it is generally very small, while the power required to drive them increases. The surfaces in fact become quite polished, and they have then no abrasive action. Messrs. Addison, Potter & Son of Newcastle-on-Tyne have long devoted considerable attention to grinding by millstones, and they build these stones of rock emery, the joints being run with a special mixture of cast iron. Provision, if required, is made for furrows, but for many purposes these stones work very well without them. Of course, the surfaces cannot be touched by any tool, but as a matter of fact they do not require dressing or levelling. Nor do the surfaces polish, and these millstones will work effectively during their whole life, which is much longer than in the case of stones built of French burrs.

It only becomes necessary to put them out of work when it is required to attend to the neck of the spindle, or to lower the cross-bar in the runner, and to cut away the centre part of the bedstone and the swallow of the runner, for which purpose these parts are constructed of French burrs. The rough abrasive surfaces of the emery blocks render them particularly suitable for grinding core from sieves or from separators, while Messrs. Potter themselves employ them for double-grinding cement to an extreme degree of fineness, an operation which is practically impossible with French burr stones. The clinker is, to begin with, finely crushed, then passed through the first set of mills, which grind it

so fine as to leave a residue of from 5 to 10 per cent. on a test-sieve of 50 meshes to the lineal inch; finally, without any attempt at sifting, the meal is passed through the finishing stones, which are built specially for fine grinding.

Our own experience with these millstones, both for grinding clinker and raw flour from hard limestone, has been entirely successful. Except for grinding slurry, their use in the Thames and Medway district has not been large, but in the north of England, in cases where millstone grinding is still practised, they are employed to a considerable extent, frequently in connection with air separators.

Continental Practice.—This for many years followed English methods, millstones being largely employed. Sifting was, however, introduced abroad at an earlier date than in this country. In England the almost universal practice is to make the upper millstone the revolving one or runner, and mills of this type have been largely used on the Continent, but in many cases those with under-runner stones, the upper one being fixed, are preferred abroad. It is claimed that a larger output can be obtained from these mills than from those with over-runners, as the material in course of being ground, which falls upon the rapidly revolving stone, is by centrifugal force thrown towards the periphery.

The ball-mill has likewise been extensively used in Germany as a fine grinding mill, for which purpose, as we have previously mentioned when considering the dry process, it is not well adapted owing to the small output. In some cases it was customary to grind coarsely with ball-mills, the product being sifted through fine sieves, and the residue returned to the mills for further grinding with fresh clinker. Such mills have also been used for finely crushing clinker previous to grinding by millstones.

Experiments with Grinding Machinery of other Types.—It was once a common saying that English cement was more coarsely ground than German, the probability being that both coarse and finely ground was made in both countries and that the purchaser got what he paid for. Whatever may be the truth, it cannot be said that strenuous attempts were not made by English manufacturers to devise a better method of grinding than by millstones. Many different forms of mill were tried and large sums of money were wasted in fruitless experiments. At one time high-speed machines acting by percussion were favoured. Many of these would grind finely and give a large output, but one and all of them speedily wrought their own destruction. The cost of repairs and renewals was so great that their use was abandoned, and mills of this type have practically disappeared from the cement industry in Europe. We notice, however, that an attempt is at present being made to employ them in the United States of America. The ball-mill is, of course, a per-

cussion machine, but it revolves at a low speed, and this makes all the difference.

The Roller-mill.—Some instructive and valuable experiments were carried out in 1880 in Germany at the Quistorp Works by Dr. Tomei with roller-mills, details of which have not, we believe, hitherto been published in this country, but which will serve to put the case of rollers *versus* millstones in the best possible light. The mills with steel rollers were specially constructed for grinding cement, and the material made use of for the tests consisted of the coarse hard particles of clinker rejected by the sieves. Two pairs of freshly-dressed burr stones, 4 feet 3 inches in diameter, and running at from 110 to 115 revolutions per minute, yielded on the average of a nine hours' test 8·5 tons of cement per hour, ground so fine that the residue on a sieve with 5,806 meshes to the square inch was only 16 per cent. Twenty-three horse-power was indicated by careful brake experiments, and the temperature of the meal rose from 117° to 192°.

Exactly the same amount of power sufficed in the parallel experiment to drive two sets of rollers and one pair of similar stones; the yield from the rollers was 14·5 tons per hour with a 13 per cent. residue on the sieve of 5,806 meshes per square inch. No observable rise of temperature took place in the grinding and in connection with prolonged use of the rollers; it is stated that after four months working they showed no signs of wear, except that the outer edges were somewhat chipped. The total width of the rollers was 19 inches, but, beyond the fact that they were driven at differential speeds, to attain a certain amount of rubbing action, combined with the crushing, which produced a softer meal, no details of the mechanical arrangements are given.

The above series of experiments were moreover valuable in that they afforded reliable data respecting the comparative strength of the two samples of cement produced by milling and crushing. In order to test this question thoroughly, samples of the material produced in either way were carefully checked by the sieve and made into briquettes neat and with standard sand. The cement from the stones left a residue on the sieve with 5,806 meshes to the inch of 15·74 per cent., and on a sieve with 32,275 meshes to the inch a residue of 21·15 per cent.; the total of the coarse particles from both sieves being thus 36·89 per cent. The following table shows the tensile strength of the cement in lbs. per square inch neat and with three parts of standard sand:—

	7 days.	28 days.
Neat,	428·1	480·7
1 to 3 sand,	173·5	240·1

A sample of exactly the same cement produced by the roller-mill left a residue on the 5,806 mesh sieve of 13·63 per cent., and on the 32·257

mesh sieve of 23·44 per cent., or a total residue of 37·07 per cent. The tensile strength, tested as before, was as follows:—

	7 days.	28 days.
Neat,	378·4	492·3
1 to 3 sand,	163·6	251·8

It appears from the figures that though the results were a little in favour of the stones at seven days, the twenty-eight days' test gives the advantage to the rollers, and we may take it that, so far as the quality of the cement is concerned, there was practically no difference whatever in the two products.

It will be observed that the grinding was equally fine, but it is pointed out by Dr. Tomei that while the millstone-ground cement steadily deteriorated from hour to hour, owing to the wear of the dress on the stones, the cement produced by the rollers manifested latterly a slight improvement in quality. The rollers were most accurately turned and polished, and were set so fine and true that a sheet of notepaper, when passed through them, was marked equally on both sides.

Similar Results have not been obtained in England.—These tests certainly explain the reasons for the confidence at one time expressed by foreign manufacturers in the roller-mills, but we cannot find that any results approaching these in excellence have hitherto been attained in this country. In fact, the following letter received from an eminent English firm at Halling puts a very different light upon this process of grinding:—

“We may say that some years ago we erected, at great cost, a complete and most elaborate system of (German) roller plant on most approved principles. It was a complete failure. It certainly ground the cement to the required fineness on the 50 and 80 mesh tests, but the difference in the comparative strength of the same clinker, prepared by stones alone in the ordinary way, and that when done by the roller plant, was most apparent. Fully one-third less strength neat, and more still when tried with the standard sand test. The setting was always slow, even with an otherwise quick-setting sample. No difference could be ascertained in the appearance or shape of particles under powerful microscopes.”

“After litigation the German firm of engineers replaced the rolls by millstones, and this gear was only recently taken out and replaced by massive English-made stone gear. The real cause of the failure was the want of flour or impalpable powder in the same proportion as that produced by friction-ground stuff through stones.”

“It was very fine stuff as a whole, but this flour was wanting, and 80 per cent. or more was really only very fine residue, which acted like

sand, and so retarded the setting. Sifting on a 30,000 mesh sieve, or through silk gauzes, told the tale; and these fine sieves are really the only ones that should be used in classifying or testing the values of cement meal."

"Since our experience of these rolls, we have always thought that this flour could only be produced by frictional grinding, but last year we saw an English edge-runner mill, and tested the same, and found that the flour was equal to that ground through the stones. The tests were also equally good, so there are hopes of the clumsy stone method being superseded. These other systems all take less power than stones."

"Some German friends, who spoke so well of the rolls before we put them down, never had found out our cause of failure until they heard of it here, as it had previously been their habit to mix into one conveyor the product from the rolls and stones, and so the fault had not made itself apparent. We believe that their idea now is the same as ours, and they are agreed that roller-plant without stones will not do, although they can be worked in conjunction with each other. The system was so elaborate, complicated, and expensive, that we preferred to simplify the process, and to do away entirely with the rolls, and not even to have a 'joint-plant,' and we learn that in certain factories abroad, where the rollers were formerly in use, they have reverted to burr stones."

Edge-runner Mill of Dutrulle & Solomons.—Mills of the edge-runner type have been largely experimented with and used in this country, and results of their working have from time to time been published. Among these, Dutrulle & Solomons' mill, Neates' Dynamic Grinder, and Freeman's Hydraulic Grinder, have been most extensively employed, and may here be noticed. In the first-mentioned mill the runners, four in number, are vertical, and revolve in different paths. The material to be ground is fed upon the upper one, and by the action of scrapers it is carried down to the lowest level, from which it is delivered to elevators. These conduct it to a sieve, which separates the fine and coarse portions, the latter passing back again to the mill to be re-ground.

The runners weigh about 6 tons each, and are built up of specially hard iron, the weight being obtained by cement filling. The beds are similarly constructed of hard iron—in fact, the manufacturers assert that these mills will grind 10,000 tons of cement before the wearing parts need renewal. These results are attained by the selection of specially tough iron, and by the great thickness ($1\frac{1}{2}$ inches) of the metal. It is claimed, moreover, that the grinding is effected rather by the rubbing together of the masses of clinker than by the contact with, and consequent abrasion of, the metal surfaces.

It was found in the course of some trials at Messrs. Booth's works

near Rochester, that 40 I.H.P. was required to drive this mill for an output of 39½ cwt. of cement in half an hour, or at the rate of about 10 I.H.P. per ton per hour. During this experiment the amount of material returned to be re-ground with a sieve of 150 meshes to the lineal inch was 40 per cent.; with an 80 mesh sieve, 24 per cent.; and with a 50 mesh sieve 12½ per cent. The mill was driven at 20 revolutions per minute, the engine running at 65. The ground cement had a weight of 117 lbs. per bushel. In all mills of this type, our experience shows that the character of the meal produced differs from that yielded by burr stones, and manufacturers who have this mill in use have, we understand, found some difficulty in turning out a cement of high tensile strength.

In a circular issued by the manufacturers, some trials of this mill are compared with the results obtained by millstones. The output per hour is here stated to be 4 tons, ground to a fineness of 5 per cent. residue on a 50 by 50 sieve, the net indicated horse-power required being 60. The case of millstones is, however, not fairly put. In one instance, the product from a pair of 4 feet 6 inch millstones, ground to the same fineness, is given as 15 cwt. per hour; in another, as only 12 cwt. This is simply absurd, as we know from our own experience that, with a good sieve, 27 cwt. per hour can be regularly obtained of this fineness from hard burned clinker per pair of 4 feet 6 inch stones. It is, moreover, claimed that cement ground by these mills is of better quality than that produced by millstones, a statement which is at least open to question.

Neate's Dynamic Grinder.—In Neate's "Dynamic Grinder" four runners revolve round an inclined raceway. The clinker is in the first place crushed by powerful rolls, from which it is elevated to the storage bin, passing therefrom to the mills. From the mill, by means of a system of scrapers, which form a special feature, it is delivered to two elevators. These discharge it into two rotating sieves, the wire cloth of which is protected on its inner surface by perforated steel plates. The fine portion of the ground material is carried away by screw-conveyors, and the portion rejected by the sieves passes back to the mill.

The result of an extended trial gave a regular output of 5 tons per hour, the net I.H.P. required being 48·9, and the residue on sieves of 50 and 75 mesh being respectively 6·7 and 17·9 per cent. It is not asserted that cement ground by this method is better than millstone cement, but only that it can be in no way distinguished from it. Both the mills previously noticed are constructed for dealing with large quantities of material, but they are not adapted for fine grinding. Cement of such a coarse quality as that obtained by means of the foregoing experiments would be almost unsaleable at the present day.

The Freeman Patent Hydraulic Grinder.—This consists of a bed- or grinding-plate, three edge-runners of about 2 feet diameter by 10 inches wide, and an upper plate with a deep flange, all of chilled cast iron. The runners, by means of spindles and bearings, are attached to the flange of the upper plate, which rests on them. This plate rotates at a speed of about 50 revolutions per minute, and carries the runners round with it, travelling upon the bed-plate, upon which the material to be ground, crushed to pass a $1\frac{1}{2}$ -inch ring, is automatically fed. The flange of the upper plate shrouds the runners to a great portion of their depth, but, in addition, the whole mill is made dust-tight by enclosing it in a sheet-iron casing, which may be easily removed for inspection or repairs. Upon the top, and in the centre of the upper plate, is fixed a small hydraulic cylinder and ram, by means of which the plate and runners are forced down upon the bed-plate and upon the material to be operated upon. The grinding is thus effected by the weight of the runners and of the upper plate, supplemented by the hydraulic pressure, which may be regulated to suit material of any degree of hardness. By the action of the runners, the material traverses the runner-path to the circumference, it is swept out by scrapers, and is carried automatically to a revolving sieve, the portion rejected being returned to the mill for further grinding. The driving is effected from beneath the mill, which may be supported on suitable columns, or it may be fixed on existing millstone hursts, the stones being removed. The output is given as about $2\frac{1}{2}$ tons per hour, the cement leaving 1 per cent. residue on a 50 mesh test-sieve, and about 6 per cent. on a 76 mesh, requiring from 30 to 40 I.H.P.

Recent Practice.—We have already referred to and described the ball, tube, and Griffin mills when treating of the preparation of raw materials by dry methods. We must now consider these mills as applied to the grinding of cement. In new plants, or extensions of existing ones, the employment of either Griffin mills or ball or “Kominor” with tube-mills is almost universal, while one system or the other has in many cases displaced machinery of the kind described in the early part of this chapter. The tube-mill alone, as a fine grinding machine, without the ball-mill as a preparatory coarse grinder, has had a separate and special use.

At first only the No. 12 size was made, and the inventors adopted the wise precaution of carrying out exhaustive experiments before attempting to place it upon the market, which they ultimately did as a machine of proved value. The details were very carefully worked out, and, except as regards the manufacture of larger sizes lined with quartzite, it has undergone little if any change at the hands of the original inventors.

Introduced to the cement industry, as we have seen, about 1895, its success was immediate, as an adjunct to existing machinery. The continued demand for more finely-ground cement was pressing very hardly upon the manufacturer. It was, of course, possible to increase his grinding plant, but it was obvious that existing machinery was not suitable for fine grinding while costly experiments with other machines had been unsuccessful, and fine grinding without an increased plant meant a diminished output. It was at once recognised that the tube-mill would serve either to grind to a fine powder the core rejected by sieves or separators, or it would grind the cement direct from the mills without sifting or separating, while in either case the preliminary grinding might be much coarser than it had previously been. The result has been that in this country millstones and edge-runner mills have in many cases remained in use, being employed as coarse grinders for tube-mills. Up to the time of the introduction of the tube-mill, ball-mills were only used in this country to a very limited extent, but on the Continent, as we have previously mentioned, they were in very general use for fine grinding. All that was necessary to adapt them for working with tube-mills was to replace the fine sieves by coarser ones.

Except in cases where the original grinding machinery has been entirely replaced, few, if any, of existing cement plants which have been at work for ten years or more, are at the present time being operated without tube-mills. The result of their introduction as an addition to existing plants is either an increased output of finer cement, or the same output of finer cement with a reduced consumption of power. As an instance, two pairs of 4 feet 6 inch French burr millstones were grinding $2\frac{1}{2}$ tons per hour of cement, so as to leave 3 per cent. of residue on a 50, and 10 per cent. on a 76 mesh-test sieve; this plant required 90 I.H.P. A No. 12 tube-mill was put in with the result that one pair of stones and the tube-mill turned out $2\frac{1}{2}$ tons per hour of cement, leaving nothing on the 50, 2 per cent. on the 76, and 5 per cent. on the 100 sieve; 75 I.H.P. being required. The cement passed from the stones to the tube-mill without separation.

The coarse powder from millstones may usually pass direct into tube-mills without any separation of the fine portion. The fine cement is thus ground finer and the wear of sifting or separating plant is avoided. In some cases, especially on the Continent, the fine cement is previously taken out by air separators. With edge-runners as preparatory mills, sieves are of course necessary. The coarse cement for finishing in tube-mills should be at least so fine as to leave no residue on a test sieve of 20 meshes to the lineal inch.

Until within the last few years the Portland cement industry can scarcely be said to have existed in America and consequently most of

the plants are new. Grinding is almost universally either by Griffin, or by ball- and tube-mills; in the latter case the product from the ball-mills passes direct to the tube-mills without any attempt at separation.

Fineness of Grinding.—There is at the present time no difficulty in obtaining Portland cement of any required fineness. Much experimental work has been done in testing the comparative value of coarse and finely-ground cement, and it is now generally admitted that, as regards capacity for admixture with sand, finely-ground cement gives the best results.

An additional argument for fine grinding which has been recently advanced is that cement, which, if it were coarsely ground, would be unsound and unsafe to use, is by fine grinding rendered perfectly sound and good and this is in many cases undoubtedly true. Unsoundness and failure to pass tests may result from either incorrect proportions, coarse grinding, irregular mixtures of the raw materials, or in part from all of these causes. The resulting clinker in such cases will consist not only of the true cement compounds but also of uncombined or imperfectly combined lime. This may exist either as small fragments or in a finely-divided state, enclosed in the fused mixture of silicates. Upon the addition of water to the resulting cement, the fine particles are immediately acted upon and become hydrated, the coarser ones may be acted upon only after the cement has hardened; often after a long period of time, the result being ultimately the complete disintegration of the mass. If the cement is brought into an extremely fine state of division, the whole of the uncombined lime may be hydrated and rendered harmless before setting takes place, especially if this occurs slowly. The general tendency of fine grinding is, however, to render the cement more or less quick setting, and means have to be taken to counteract this defect by the addition before grinding of a small quantity of gypsum.

Without attempting to say a single word in disparagement of finely-ground cement, we are certainly of opinion that fine grinding of the finished material should not be employed to cover incorrect proportions and careless preparation of the raw material. Nor do we think it possible that cement prepared in this way, from which as we have seen constancy of volume and satisfactory results by means of other tests can only be obtained by extremely fine grinding, can be so perfect a material as one in which the raw materials have been carefully proportioned and prepared, even though the latter cement may be more coarsely ground. A coarsely-ground cement is not necessarily an unsound one, as will be evident by reference to the results of tests by some of the early experimenters, in cases where the fineness of the cement has also been given.

Grinding Tests.—Much work of this kind with English cement will

be found in the *Proceedings of the Institution of Civil Engineers*; many of the experiments there recorded extending over long periods of time. Constancy of volume, or soundness tests, which have only during recent years become general, are in many cases not referred to; but it may be fairly assumed that cement which continues to increase in strength with the lapse of time, and which finally shows no signs of retrogression, must have been sound and good at the commencement. Correctly-proportioned, finely-ground, and carefully-prepared mixtures of raw materials—points upon which we have throughout this book insisted—will, if properly burned, result in clinker, the cement from which, whether it may be ground coarsely or finely, will be constant in volume; the coarse or unground portion being absolutely inert.

One danger in connection with the use of finely-ground cement may briefly be referred to. If the sand is of good quality, as is usually the case on large and properly-supervised works, a less proportion of fine-cement than of coarse may be used to an equal quantity of sand with equally good results as regards the quality of the work produced and at a less cost. The proportion of sand may really be adjusted to the fineness of the cement. Large quantities of cement are, however, not used under such favourable conditions, and much of the sand employed is of very inferior quality, scarcely deserving the name of sand at all. A growing tendency exists to use increased quantities of sand, no matter what its quality may be, with the result that much inferior work is being done with very good cement.

Storing and Packing.—From the grinding mills the cement is transmitted by elevators and worm or belt conveyors to the storage bins or silos. These are generally entirely closed up while being filled, the conveyor discharging at the top, the cement thus being distributed layer above layer. It may be automatically weighed at any convenient spot on its way to the silos, the machine recording the quantity which has passed through it. In this country the usual practice is to fill and weigh the casks or sacks by hand, the floor of the store or silo being on a level with the loading platform. In some Continental works the silos form an upper storey, the bottoms of the silos being hopped and brought down to spouts, which discharge into casks or sacks on a floor at the loading level.

In many American works the packing is entirely distinct from the storage department. The bins or silos are arranged on the ground level in such a manner that they can be made to automatically discharge their contents into a tunnel common to all. A screw-conveyor running through this tunnel conducts the cement to the packing room, where it is lifted by an elevator to a hopper, from which it is drawn by spouts. Both in Continental and American works, but especially in the latter,

owing to the high cost of labour, the packing is frequently done by machine, for which purpose it is necessary that the cement should be drawn from silos or from a hopper placed overhead.

For casks it is convenient to employ a machine, which not only delivers the cement into the casks, but also, by means of a mechanical arrangement, provides that every cask shall be shaken during the filling process, so as to secure uniformity of loading. It is also possible to connect such filling machines with a standard weighing machine which cuts off the supply of cement automatically as soon as the cask has received its full charge. To prevent the escape of dust the cask is covered with a hood which can easily be adjusted by hand. By means of branched spouts it is possible to arrange for the filling of two or more casks simultaneously, all the casks being placed upon a rocking platform to shake down the contents uniformly. An apparatus precisely on the same principle has been arranged for filling bags and for weighing the contents, the supply, as in the case of casks, being automatically cut off.

Dust-Collecting Contrivances.—In whatever manner the Portland cement materials may be mechanically treated, it is impossible to prevent the formation at certain stages of the process of considerable volumes of dust, and this dust may not only become a source of danger and injury to the health of the work-people, but it may also entail a serious annual loss to the manufacturer, if precautions are not taken to keep it under control and to collect it by means of suitable contrivances. In order to separate dust from the atmospheric air in which it is suspended there are three systems available which are capable of giving good results :—(1) By the employment of filtering apparatus ; (2) by the aid of centrifugal force ; and (3) by bringing the air to rest in suitable chambers.

The first of these systems may, if properly carried out, free the air almost entirely from all the particles suspended therein. Air-filters usually consist of a number of sheets of cloth or flannel fixed in light frames, through which the air is caused to pass by an induced draught. It has been found advantageous in cement works to employ a special apparatus for filtering purposes in which the frames can from time to time, by means of taps and blows, be freed from the dust which has collected on the surface of the vertically-arranged cloths, and in which the cloth can be cleansed by reversing periodically the current of air, so as to blow out the dust from the pores. A filter of this kind has been produced by Messrs. Nagel & Kemp, and their apparatus provides a large filtering surface by arranging the frames in a cylindrical chamber, so as to radiate round a central inlet ; the dusty air passing in at the bottom, and the purified air being drawn out at the top by means of a fan. In another kind of filter, the patentee makes use of a series of

lengths of hose enclosed in a chamber; the dust-laden air passes up through the hoses and parts with the dust, which adheres to the inner surface of the hose. The portions of hose are from time to time freed from the dust by being beaten or shaken, and the pores are cleansed by reversing for a short time the direction of the air current. These hoses are arranged in pairs in air-tight receptacles, and the battery may consist of any number of pairs from one to twelve, the total height being 13 feet, and the diameter of the fans needed to work them ranging from 12 inches to 60 inches. The dust falls to the bottom of the chamber, and may either be removed continuously by a screw-conveyor, or it may be from time to time withdrawn when the hoses are being cleaned. Filters of this kind are largely used on the Continent in factories where much dust is produced.

In some cases the filter itself is made to revolve, and by this means a large filtering surface is obtained in a comparatively small space. The filter cloth is star-shaped and fixed on a rotating drum, so that separate cells are formed which are cleaned automatically by tapping. As the entire apparatus is contained within an air-tight cylindrical casing of wood or iron, it is entirely dust-proof, and it can be made to work with its own fan or with any suitable draught producer.

A filtering apparatus of a somewhat different type consists of a horizontal tube, the lower half of which is constructed of sheet iron, and the upper part of flannel or woollen cloth. The dust-laden air is passed into this tube, in which is fixed a revolving shaft furnished with spiral brushes. These brushes serve to carry the dust to the end of the tube, whence it is removed by a screw-conveyor, while at the same time they free the woollen surface from dust and facilitate the exit of the purified air.

The centrifugal system of dust collecting is much less perfect than any of those we have already described. The dusty air is admitted—in one form of machine, the “cyclone”—to an upper cylinder constructed of metal in a powerful current caused by a fan or blower. The current enters tangentially, and the dust follows the windings of a spiral until it reaches the outlet, and falls into a conical receptacle placed below the cylinder, while the air, freed from dust, escapes by an orifice in the top of the cylinder, and is usually permitted to pass up a pipe to the exterior of the building.

Under the third method of dealing with dust, the settling chambers are usually of large size, and they are arranged to occupy some vacant area in the roofs or in the upper part of the factory. These chambers may conveniently be divided into cells by a series of hanging screens or frames, covered with canvas, and for readily collecting the dust the floors are often hopper-shaped, so that the particles fall to the bottom and admit of easy removal.

Theoretically the action of such chambers depends upon the possibility of bringing the air into complete rest, and the extent to which this can be done is founded upon the relative size of the chamber as compared with the volume of the dust-laden air which has to pass through it. Even under the best conditions, this plan of freeing the air from impurities is far from perfect, but very considerable quantities of dust can be intercepted by this means, and the annual value of the cement which is obtained in this way will pay a good interest on the initial cost of constructing such chambers.

CHAPTER XIV.

THE COMPOSITION OF MORTAR AND CONCRETE.

CONTENTS.—Definition of Mortar—Action of Sand—Sand Weakens Cohesion—Opinions of Early Writers—Proportion of Sand Added—Vicat and Pasley on the use of Sand—Totten's Theory on Sand Addition—Size of Sand Grains—Scott on Proportion of Sand—Preparation of Mortar—Artificial Stone—Concrete—Armoured or Re-enforced Concrete.

Definition of Mortar.—Mortar, as the term is commonly understood in this country, is applied to the mixture of lime or cement with water to form a plastic matrix for embedding or uniting together bricks or masonry. Such mortar invariably contains a certain proportion of sand. It was an opinion very widely entertained by the earlier writers on building construction that this sand had a beneficial effect on the mortar to which it was added, though we now know that there is no foundation for this belief.

Action of Sand in Mortar.—There are perhaps certain cases in which sand of a peculiar description and used in small quantities may tend to improve a sample of lime or cement, but such cases are quite the exception, for sand can only be regarded in the light of recent experiments as a diluent, or as tending to diminish the strength of any given specimen of lime or cement, and the only valid reason that can be urged for its use is the advantage gained in point of economy by the employment of a cheaper material. It has been, however, pointed out that, when exposed to compression in mortar joints, the influence of the hard particles of sand, if duly compacted, may be beneficial, owing to the increased power of resisting a crushing strain possessed by the hard particles of quartz, as compared with the friable or putty-like mass of a pure lime mortar or even of a stratum of cement.

Properties of Mortar.—Mortar suitable for ordinary buildings must have the consistency of a creamy paste, in order to work well under the trowel into the joints and interstices of the materials. It should have considerable power of adhesion, so as to retain the substance with which it is being used in position, and it should possess the power of rapidly indurating and of becoming in course of time as hard as the remainder of the structure, which it should bind together into a species of monolith. Moreover, it should be capable of resisting the attacks of the atmosphere, moisture, and the other destructive influences to which buildings are ordinarily exposed.

Influence of Sand.—It will be obvious, therefore, that, apart from the qualities of the lime or cement, the sand which enters so largely into the composition of mortars of every description has an important function to fulfil, and though it does not increase the strength of the compound, its action upon the mortar should be carefully studied.

Sand may Act in Four Different Ways.—We may consider its probable effects under four heads. *First*, Respecting the cohesion of the particles of the cementing material. *Second*, The adhesion of the lime or cement to the surfaces of the sand grains. *Third*, The possibility of causing weak places, due to the occurrence of several particles of sand in contact without a sufficient supply of cementing material to envelope them and to fill up all the interstices; *and lastly*, the increase of strength the sand may produce in such cases in which the sand grains are stronger than the cementing material in consequence of the line of fracture being longer than it would be if no sand particles were present to interrupt the direct passage of the fracture in one plane.

Sand Tends to Weaken Cohesion of Mortar.—Treating of these various points *seriatim*, we know from numerous tests, conducted by skilled observers, with every description of lime and cement, that the cohesion of the particles of mortar made from neat lime or cement is nearly always greater than that which is found to exist between the particles of the same cementing material when used with sand. If we regard the matter simply as one of cohesion or adhesion, though wide differences doubtless exist between the behaviour of various qualities of sand, whether the surface of the grains be rough or smooth, or whether the lime or cement be capable or incapable of exerting a chemical action upon them, the general effect of sand, which retains its position in the mass by the force of adhesion only, is to lessen the force of cohesion. The diminution of strength will be greater in the case of fine sand than it will when coarse or large-grained sand is employed, and it will invariably be larger in direct proportion to the amount of sand we use. For in both these cases the surface to be covered with the cementing agent is enlarged. We substitute, in fact, a lesser force, that of adhesion, for a greater force, that of cohesion, the more sand we add. To the same extent, also, that we increase the amount of sand, we incur the risk of weak points from a deficiency of cementing material. The only benefit we can trace then to the employment of sand is the interposition of the sand grains into the direct path of fracture, which they tend to lengthen and increase, and in so far as these grains are stronger than the lime or cement we are using, they may improve the mortar.

Sand does not, therefore, improve the Mortar.—On the whole the advantages of the sand do not counterbalance the sources of weakness introduced by it into the mortar, and practical experiments confirm the

truth of these views. Mortar is, in fact, merely rendered cheaper by the employment of sand, but not in any sense improved by its use.

Opinions of Early Writers on Sand in Mortar.—From the time of Vitruvius onwards all writers on the subject appear to have taken it for granted that a due admixture of sand must tend to improve the mortar. The earliest builders no doubt found that lime used alone, especially in the form of stucco, had a tendency to shrink and crack in drying, and that this failing could be corrected by the addition of a certain proportion of sand. Having once established this fact, we can well understand that it soon became a settled doctrine that the use of sand was a matter of necessity in the production of a good sample of mortar, but it is strange to find how greatly opinions have differed respecting the reasons for the beneficial effects of this addition, and with regard to the proper proportion of sand to be employed.

Proportion of Sand Added.—Vitruvius asserts that “when the lime is slaked it is necessary to mix 3 parts of sand, if the sand is fossil (pit sand), with 1 part of lime; and if the sand is river sand to add 2 parts of it to 1 of lime.” He goes on to say that these are the best proportions to use for mortar, and he accounts for the hardening of the mixture somewhat ingeniously as follows:—“The weight of the lime after calcination is diminished about one-third by the evaporation of the watery parts; from this it results that the pores being empty they are better fitted than before to receive the admixture of sand, and to unite strongly with the blocks of stone to form solid masonry.”

Theories for Use of Sand.—Many authorities, ancient and modern, follow Vitruvius and adopt his views; some of them endeavour to invent equally fanciful theories to prove the advantages conferred by the sand. Thus Macquer states that “the particles of slaked lime adhere more closely to hard bodies than to each other, on account of the great quantity of water united to them, which prevents their coming so closely into contact as they do with sand or cement (puzzuolana), for these substances by absorbing a portion of the water of the slaked lime facilitate the drying and adhesion.” The amount of water absorbed by sand would be infinitesimally small, and this theory is manifestly incorrect, though it has some show of reason in its favour.

Invariable Rule Established to Add Sand.—It gradually became recognised as an established fact among builders that lime was capable of taking up a prescribed dose of sand (the amount assumed to be the correct proportion varied greatly), and it was not until Vicat and the careful experimenters of the French school, and our own countrymen, Smeaton and Pasley, began to conduct independent tests that the old faith in the efficacy of sand began to be shaken.

Proper Proportion of Sand to be Used.—In the matter of propor-

tions there has been at all times a great difficulty in deciding exactly what was really intended by writers upon this subject. Some authorities made their mixtures by weight, some by volume, some used lump lime, and others used slaked lime, so that no two results are strictly comparative. The views of Smeaton on the employment of sand are sound and good. He states that: "The use of sand in mortar, so far as I have been able to observe, is two-fold—1st, to render the composition harder; and 2nd, to increase it in quantity by a material that in most situations is of far less expense, bulk for bulk, than lime. As there is no apparent change in the sand by the admixture of the lime, the sand seems only to render the composition harder, by itself being a harder body; for the best sand being small fragments of flint, crystal, quartz, &c., is much harder than any body we know of that can be formed of lime only, which in paste is to be considered as a cement to the harder material, and therefore composes a harder body; for the same reason that if we had nothing naturally but lime as a cement, and should build a wall with flints, crystals, or rough stones cemented therewith, this wall would be harder than if built with lime alone."

Vicat on the Use of Sand.—Vicat, whose experiments on cement were, as we have seen, more careful and elaborate than those of most of his predecessors, cannot be trusted when he deals with the question of sand addition, for he could not in this case shake off the trammels of routine, and he accordingly regarded sand as a necessary part of mortar. He, however, lays down rules for the proportions of sand to be employed with fat and with hydraulic limes, which show a sound appreciation of the subject, and he points out that the quantity of sand must vary in accordance with whether the mortar is to be used in exposed or in protected situations. He asserts that the "intervention of pure sand does not tend as was before believed to augment the cohesion of which every kind of lime indifferently is susceptible, but it is injurious to rich limes, very serviceable to the hydraulic and eminently hydraulic limes, and is neither beneficial nor injurious to the intermediate kinds."

Pasley's Rules for Use of Sand.—Pasley, whose protracted investigations into the nature of cement mixtures and the influence of sand are so well known, did not fully recognise the facts of the case, for he seems to have thought that the strength of mortar was in some way or other related to its plasticity or pleasantness in working. He tells us that he found that Halling lime would not stand so large an addition of sand as the common chalk lime, and he proceeds to state, "every one will acknowledge that the proportion of sand which will make good mortar with chalk lime would entirely ruin cement, which is scarcely capable of bearing one-third of that quantity." Of course he had in view the Roman cement of those days which will take but little sand; but he

spoke from the workman's point of view, and regarded a mortar as ruined when it was "too short for use." We now know that Portland cement will make a strong mortar with six volumes of sand, though few workmen care to use it when mixed in these proportions.

Totten's Theory as to Sand Addition.—We do not find any writer on this question who is entirely to be trusted until we come to the experiments of General Totten, who employed a pure fat lime, and who clearly shows that each increase in the proportion of sand involves a falling off in the strength of the mortar; the lime alone furnishing the strongest mortar. His experiments, are set forth in the following table, which we have extracted from the valuable essay of General Scott, published in vol. xi. of the Professional Papers of the Corps of Royal Engineers:—

NATURE OF LIME.	COMPOSITION OF MORTAR. THE LIME MEASURED IN PASTE.						
	0 Sand. 1 Lime.	$\frac{1}{2}$ Sand. 1 Lime.	$\frac{1}{2}$ Sand. 1 Lime.	1 Sand. 1 Lime.	2 Sand. 1 Lime.	3 Sand. 1 Lime.	4 Sand. 1 Lime.
Smithfield fat lime, .	262.5	245.6	222.5	214.7	170.3	154.6	135.1

The lime used in these tests was carefully ground in a mill and the mortars were moulded into prisms 6 inches long by 2 inches square in section. They were then subjected to a pressure of 600 lbs. for a few minutes, and after 50 days were broken by a force acting midway between the points of support, which were 4 inches apart. Three trials were made of each sample, and the highest breaking weight is in each case recorded. In all the experiments made by Totten he found that the strength of the mortar diminished as the quantity of sand was increased.

Importance of the Size of the Sand Grains.—The size of the sand grains and the proportion of solids to voids in any given sample of sand is no doubt a subject of much importance in making mortar. It is a matter of common knowledge that if a measure of known size be filled with dry sand, and if water is then poured upon it, the sand will settle down as the water is steadily added, and owing to a re-arrangement of the sand grains the mass will ultimately occupy a greatly reduced volume to that which it does in the dry state. Under certain conditions this shrinkage may amount to 25 per cent. of the volume. In the course of some experiments at Bermuda by Colonel Nelson, R.E., it was found that 1 part of lime powder when added to 3 parts of sand scarcely sufficed to fill the voids. In the form of paste it took 1 part of lime paste to fill the voids in 6 parts of sand.

The general experience is that coarse grained angular sand produces a tougher and stronger mortar than a very fine grained sand, though the

latter works more sweetly under the trowel. This is probably due to the larger air spaces caused by the cavities or voids of relatively larger area. The average voids in sand have been found by careful measurement to amount to about 33 per cent. of the total volume occupied by it. No mortar can be regarded as wholly satisfactory in composition in which the voids in the sand are not filled up by the cementing material, because otherwise certain of the grains might be in contact and have nothing between them, to hold them together.

Scott on Proportion of Sand to be Used.—General Scott, as the result of the careful consideration of numerous specifications, comes to the conclusion that if we are using the feebly hydraulic gray chalk lime, such as is generally employed in the London district, we may safely add $1\frac{1}{2}$ parts or even 2 parts of sand to 1 part of slaked lime by volume. With a more hydraulic lime, such as that obtained from the lias formation, he would use 2 parts of sand to 1 part of slaked lime; and with the pure chalk lime or the fat lime resulting from the calcination of a pure limestone, since the mortar so obtained is at all times very inferior, he states "if we are compelled to use such miserable stuff we shall not be losing much in resistance if we increase the quantity to 3 parts of sand to 1 part of lime."

The Preparation of the Mortar.—All the earlier writers on mortar laid great stress upon the thorough incorporation of the lime and sand, and it would seem by the price-books of the last century that in this country it took quite a day for a labourer to beat together the ingredients necessary to make 1 cubic yard of mortar. At the present time in all important works the mortar is mill-made, and in this way, no doubt, a far better mixture of the sand and lime is obtained than by the old-fashioned system of beating or larrying.

Experiments on the Strength of Mortar.—Many writers have experimented on the strength of the various descriptions of mortar, and it is not our intention to go into this question more in detail in the present chapter, as we shall have to revert to this branch of the subject in our chapter on cement testing.*

Concrete.—We have still to deal with the question of concrete, a term of recent origin, which has been considered by some authorities to be derived from the Latin word *concreasco*. This may be taken to mean to grow together, or to consolidate. By "concrete," or the French word "*béton*," is meant a conglomeration of small stones embedded in a matrix of cement or mortar. There are natural examples of concrete in the "pudding stones," where gravel pebbles are united together by oxide of iron, or some similar binding agent, into a hard mass. Building with

* In Appendix A (folding table) will be found some experiments by Mr. Kirkaldy on various descriptions of mortar.

factitious stone was in use in very ancient times, and some writers have asserted that certain of the Pyramids of Egypt were constructed with artificial blocks of small stones and lime. Many of the earliest buildings in this country, dating back to the time of the Roman occupation, were evidently constructed of a species of coarse rubble-work, wherein fragments of stone and flint are embedded in lime mortar.

Artificial Stone.—As the knowledge of the properties of cements became extended, it soon occurred to ingenious minds that these materials might be employed in the formation of artificial stone, and this idea was first worked out upon a practical scale in France. Towards the close of the eighteenth century several inventors made known their processes for moulding a mixture of cement, sand, and gravel. The first experiments in this direction appear to have been due to a Toulouse architect, M. Lebrun. He used a specially prepared cement, which he made in a lime kiln; this cement, to which he gave the name of "hydro," was composed of a mixture of lime, clay, and powdered coke or charcoal. The calcined material was ground and mixed with varying proportions of sand into a very stiff paste, with a minimum of water. This paste was at once introduced into the moulds and well rammed with a beetle. The artificial blocks made in this way were sometimes of a considerable size, and arches, with a span of upwards of 30 feet, were constructed under Lebrun's system.

Ranger's Concrete.—In this country the concrete constructions of Mr. Ranger, about the year 1832, for which he obtained patents in December, 1832, No. 6341, and again in 1834, No. 6729, attracted considerable attention. The wharf wall of Woolwich Dock Yard was erected by this process, and its subsequent failure, due rather to insecure foundations than to a defect in the material, for a time brought concrete work into discredit.*

Vicat, in his work on mortars, describes a rude system practised in Piedmont for the production of artificial blocks of stone. Pits or trenches are excavated in a stiff clay soil to a depth of about 4 feet, and the sides are carefully trimmed to the requisite dimensions, and thus constitute a species of mould. A mixture of hydraulic lime and sand is then introduced, and large pebbles are inserted by hand in such a way as to cause the compound to be driven into all parts of the mould, the top is levelled off with a trowel, and then the whole mass is carefully covered over with about 2 feet of soil, and left for two or three years to become indurated. The lime used for this purpose is obtained at Casal, and is one rich in magnesia. The blocks formed in this way in a damp soil obtain a surprising degree of hardness, and may be dropped one on to the other from a height of 20 feet without injury.

* See Pasley's work, p. 21; and again in his Appendix, p. 30.

Concrete in France and England.—In consequence of the inventions of M. Coignet in France, and of Mr. F. Ransome in this country, increasing attention has in recent times been paid to the production of monolithic structures formed of gravel or ballast, aggregated together into masses by means of lime or cement. Concrete is really a mortar matrix, serving to bind together a suitable proportion of pebbles, flints, or broken stones. The amount of lime or cement to be used in making concrete must thus be to a certain extent determined by the nature of the materials to be employed as aggregates. It ought theoretically to consist of a perfectly made mortar, sufficient in quantity to fill the voids of the larger materials, for which it is to be used as the incorporating medium. The proportion of lime or cement may vary from one-seventh to one-twelfth of the aggregates, but no concrete can be really sound and good where the materials—the sand and gravel—are not properly adjusted. We mean by this that the lime or cement should be sufficient to amply fill the interstices of the sand, and the lime and sand mortar should properly fill the voids in the larger masses of stone. It has been found by careful measurement that while the voids in pebble-gravel will average about 34 per cent. of the volume it occupies when dry, the voids in broken stone may average from 40 up to 50 per cent. of the volume. Taking a mortar composed of 1 part of cement to 3 parts of sand, we might safely add, for the purpose of concrete-making, 3 parts of gravel to 1 of mortar, or 2 parts of broken stone. In some specifications, however, these limits have been dangerously exceeded, and there is sometimes a failure to apportion properly the sand and the larger aggregates. When concrete is merely used as a material for foundations in trenches this is not a matter of very great importance, but where the concrete is to be used moulded into blocks, or in order to form monolithic structures, it is very necessary to study these matters with care.

Experiments of Mr. A. F. Bruce on Concrete.—The observations of Mr. A. F. Bruce, who has carried out numerous experiments respecting the strength of Portland cement concrete, and whose investigations are published in vol. cxii. of the *Min. of Proceedings of the Inst. of Civil Engineers*, will show the importance of attending to these details. By careful manipulation of the ingredients and accurate adjustment of the proportions some excellent specimens of concrete known as "*bétons agglomérés*" are produced in France, and have been employed for very numerous purposes, for which stone or terra cotta is used in this country.

Cement and Concrete Mixing by Machinery.—Machinery has in recent years been introduced into all large works for the preparation both of mortar and concrete, to supersede the former slow and cumbrous method of hand-mixing. In the case of mortar-making many advantages are no doubt obtained by the use of edge-runner mills of sufficient size,

especially where lime has to be incorporated with burnt ballast. In the case of cement mortars the employment of the ordinary mill seems to have a tendency to decrease the tensile strength of the mixture, and to retard somewhat the initial set of the cement, but if, for cement mortars, the rollers are taken out of a revolving-pan mill and replaced by a fixed arm with teeth, a very effective mode of mixing is secured, which greatly surpasses hand-gauging. For the preparation of concrete, numerous mechanical devices are available, all of which are immeasurably superior to hand labour, for in all of them a very intimate admixture between the cementing material and the gravel or ballast is secured, and great uniformity in the adjustment of the proportions is attained. In order to produce the best results, a careful study of the voids in the sand, as also in the substances to be concreted together, is, as already stated, indispensable.

Armoured or Reinforced Concrete.—The employment of concrete in construction is now making vast strides owing to the enormous gain in strength which is attained by the judicious use of an iron or steel core, or in the case of slabs or thin blocks, by the employment of wire netting or perforated iron plate, the so-called "extended metal." The weight of iron which was formerly introduced in the shape of rolled joists, for instance, in flooring, has been proved to be quite unnecessary, and it suffices to employ twisted rods of small section, embedded in the centre of the concrete, to impart a degree of strength which is greatly in excess of that which would pertain to the sum of the strengths of the concrete and of the rods used separately. Experiments tend to prove that in armoured concrete the iron core acts in tension, while the concrete clinging round it is in compression. The subject of reinforced concrete, which has been much studied, both on the Continent and in America, must be reserved for a future volume.

CHAPTER XV.

CEMENT TESTING.

CONTENTS.—Early Cement Tests—Their Doubtful Value—Pasley's Tests—French Tests—Grant's Tests—Briquette Making—Early Specifications for Cements—Cost of Testing—Defects in mode of Testing—Specific Gravity Test—Form of Test-Briquettes—Instructions for Testing by Mr. Grant—Professor Unwin on Cement Testing—Induration of Cements—German System of Testing—Adie's Testing Machine—The Goreham Flourometer—Arnold's System of Testing.

Early Cement Tests.—The makers of the quick-setting cement of the Roman cement type were fond of displaying the tenacity and tensile strength of that material by the construction of horizontal beams of brickwork, which were built out from a wall a brick at a time. Sometimes a whole day was allowed to elapse between the placing of each brick; at others the fresh bricks were added as soon as the last made joint had become set. For this purpose some five or six minutes would suffice with the best quality of Sheppey cement, and General Pasley observes: "It was stated in my presence at one of the meetings of the Institution of Civil Engineers, by members of that Society, that so many as thirty bricks had been stuck out in one day, and thirty-three bricks in thirty-three days in the same manner." Messrs. Francis had similar beams at their works, and General Pasley tested his artificial cement both by building out the beams with the bricks laid horizontally, and also with the bricks arranged in a vertical position, in which latter case a far greater number could be supported.

Doubtful Value of these Tests.—He says, when speaking of this system of testing: "Considering that this mode of setting out bricks from a wall, though an excellent test of the quality of different sorts of cement, if always done under the like circumstances, might be supposed doubtful, if executed by workmen of unequal skill, or not precisely in the same manner, and in different states of weather or of temperature; and considering also that a pier [beam] of this sort, exhibited at the premises of any cement manufacturer, might not be considered satisfactory by persons who had not been actually present at the time the bricks were placed; since there can be no doubt that, by permanently supporting such piers for several months, a much greater effect would be produced than by the mode I have described of only holding each successive brick a few minutes by a trowel; it therefore appeared

desirable when we first prepared for commencing those experimental piers [beams], to make arrangements also for trying the comparative strength of the same from artificial mixtures by tearing them gradually to pieces by a dead weight."

General Pasley's Tests.—He then describes a plan of uniting three (afterwards four) bricks together on the flat by two joints of 9 inches by $4\frac{1}{2}$ inches, having mortises cut in the upper and lower bricks for receiving iron nippers. After allowing from thirty-six to forty-three days for the induration of the cement, the joints were torn asunder by gradually applied weights, laid on by $\frac{1}{2}$ cwt. at a time, in an apparatus which was in the nature of a gigantic scale-pan. It was found that when only three bricks were used the weight generally fractured the uppermost bricks by tearing them apart at the mortises, so that in the later experiments four bricks were used, and the mortises were cut in the top and bottom bricks, by which means the solid part above and below the mortises is strengthened by the thickness of one entire brick and a cement joint, leaving the centre joint only exposed to the full action of the breaking apparatus.

Unscientific Nature of the Early Cement Tests.—All of these tests, and even those obtained in later times by joining two bricks together crosswise, so as to obtain a cement or mortar joint $4\frac{1}{2}$ inches by $4\frac{1}{2}$ inches = $20\frac{1}{4}$ square inches in area (see Fig. 46), were far from scientific, and it was not until recent times that the more accurate and reliable system of using briquettes, having a standard area at the neck or point selected for fracture, came into use. These notched briquettes appear to have been first used by French engineers. For an early test of Portland cement briquettes of this kind, see the experiments at the 1851 Exhibition, p. 40.

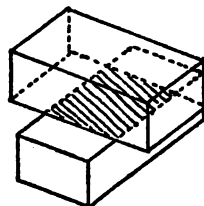


Fig. 46.—Bricks joined crosswise for Cement Testing.

The Value of Portland Cement made known by Testing.—The estimation in which Portland cement is at present held, the reputation it enjoys among engineers, and indeed its high position as a building material are mainly due to the tests it has undergone in the past, and to its behaviour under others of like character and of increasing severity that are constantly being applied to it. It was pointed out many years ago at the Institution of Civil Engineers that, in introducing a cement of this nature, it was very necessary to adopt some general standard of excellence, and the first record we can find of any systematic experiments with Portland cement were those conducted by the *Ingénieurs des Ponts et Chaussées*, by whom this material was employed on a large scale about 1848 to 1850.

Early French Tests of Portland Cement.—The French tests in use at that period were in the main as follows:—

Specific weight 1,200 kilogrammes per cubic metre, or 96 lbs. per imperial bushel.

Tensile strength of briquettes on the area of 2.25 square inches.

Neat Cement.				1 Cement to 2 parts Sand.			
	Kilogrammes.		Lbs.	Kilogrammes.		Lbs.	
In 2 days, . . .	64	=	141	...		...	
„ 5 „ . . .	128	=	282	64	=	141	
„ 30 „ . . .	240	=	528	128	=	282	

Tests by Mr. Druce and Mr. Rendel.—Very shortly after this date Portland cement was used extensively on English harbour works by Mr. Rendel and by Mr. Druce at Holyhead and Dover, and these gentlemen subjected the material to searching tests, but it does not appear that its compliance with any definite standard was at that time insisted upon.

Mr. John Grant's Tests.—The engineers of the Metropolitan Board of Works were the first public officials in this country to institute analogous tests to those adopted in France, and to the late Mr. John Grant, M.Inst.C.E., who was mainly responsible for these tests, and who on several occasions presented to the public the results of the long and laborious investigations carried out by him respecting the strength of Portland cement, we are largely indebted for our present knowledge of the properties of this material, and for the vast improvements which manufacturers have been able to effect in its quality of late years.

Mr. Grant's Essay on Cement in 1865.—In a paper entitled "Experiments on the strength of cement," communicated to the Institution of Civil Engineers in December, 1865, Mr. Grant described the steps taken by him during the construction of the southern portion of the Metropolitan Main Drainage Works, in order to ensure the use of cement of the best quality only. He points out that previous to 1859 Roman cement was with but few exceptions employed for the inverts of the London sewers, the arches being set in blue lias lime, and Portland cement being "scarcely ever tried." It was, in fact, until this time chiefly employed as a stucco, and in ordinary building operations, though it had been, as we have seen, used at Dover and elsewhere mainly for the formation of concrete blocks, and it had already been largely adopted abroad.

Mr. Grant's First Specification Based on Tests.—After some preliminary tests with samples of cement procured for the purpose from various manufacturers, and some corresponding trials of cement obtained from the makers in the ordinary way, the following clause was inserted in the specification for the Southern high-level sewer, dated 1859, being

the first contract under the Metropolitan Board of Works on the south side of the River Thames :—

“The whole of the cement to be used in these works, and referred to in this specification, is to be Portland cement, of the very best quality, ground extremely fine, weighing not less than 110 lbs. to the struck bushel, and capable of maintaining a breaking weight of 400 lbs. on an area $1\frac{1}{2}$ inches by $1\frac{1}{2}$ inches, equal to $2\frac{1}{4}$ square inches, seven days after being made in an iron mould of the form and dimensions shown on drawing (see Fig. 47), and immersed six of these days in water.”

Briquette-moulding Machine.—In order to prepare the requisite test-briquettes, a moulding machine of simple construction was introduced, and bell-metal moulds, having a sectional area of $1\frac{1}{2}$ inches by $1\frac{1}{2}$ inches at the breaking point, were employed. The moulds were originally provided with linings or templates of thin iron, which exactly fitted them and enabled the briquettes to be removed directly they were formed. The moulding apparatus, as also the testing machine, were made by Mr. P. Adie, and these appliances were speedily adopted by all cement manufacturers as well as by most large users of cement, while this system of testing soon became the recognised plan of judging the quality of cement throughout the country.

Tests made by Ordinary Workmen.—No difficulty was experienced in training an ordinary workman to carry out these tests, and the process was found to answer well in the case of the 70,000 tons of Portland cement used during the construction of the first portion of the outfall works.

Objections to Severity of Test by Manufacturers of Cement.—It seems now somewhat strange to read that in the first instance objection was taken by manufacturers to the standard then proposed of 400 lbs. tensile strength to the $2\frac{1}{4}$ square inches, and it was urged that 300 lbs. would be the highest attainable strength in actual practice. It was soon found, however, that this was not an unduly onerous stipulation for the cement trade, and indeed it shortly afterwards became possible to raise the tensile strength considerably. Thus the clause already given was amended, so that the tensile strength demanded was 500 lbs., and the contractor was compelled to keep in store upon the works “a supply of cement equal to at least fourteen days’ requirements,” and with each delivery of cement he was to “send to the clerk of the works a memorandum of the number of bushels sent in, and the name of the manufacturer.”

Modification in Specification about 1865.—Ultimately, about 1865, the clause was again amended, when it read as follows :—“The

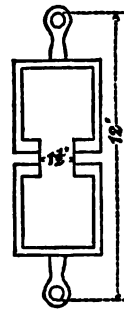


Fig. 47.
Mr. Grant's
Original Test
Briquette.

whole of the cement shall be Portland cement of the very best quality, ground extremely fine, weighing not less than 112 lbs. to the struck bushel, and capable of maintaining a breaking weight of 250 lbs. per square inch (562.5 lbs. on $2\frac{1}{4}$ square inches), seven days after being made in a brass mould, and immersed in water during the interval of seven days. The contractor shall at all times keep in store upon the works a supply of cement equal to at least fourteen days' requirements; and with each delivery of cement shall send to the clerk of works a memorandum of the number of bushels sent in, and the name of the manufacturer."

Tensile Strength again Raised before 1870.—Before 1870 the standard strength was again raised, and in the specifications for the Southwark Park and subsequent works it was stipulated that the cement should be "capable of maintaining a breaking weight of 350 lbs. per square inch" (787 lbs. on the breaking area of $2\frac{1}{4}$ square inches), tested as before. Thus in a little over ten years the standard strength had been nearly doubled, and from the tables given by Mr. Grant it would appear that many samples were considerably in excess of the specified requirements; the Burham Company having supplied over 320,000 bushels, showing an average breaking weight of 825.73 lbs. on the $2\frac{1}{4}$ square inches; even these figures having been exceeded by certain other makers who furnished smaller quantities of the material.

Cost of Cement Testing as Carried out under Mr. Grant.—It is interesting to notice these facts as bearing upon the steady improvements made in the quality of Portland cement. Mr. Grant states that the entire cost incurred in testing the cement furnished during a series of years to the Metropolitan Board, during which period works to the value of upwards of £1,250,000 were executed, was about five farthings per ton of cement.

Defects in the Present Mode of Cement Testing.—It is somewhat unfortunate that the tests first adopted in this country, and which have thus furnished the precedent for the majority of engineering specifications, from the fact of their being carried out with neat cement, fail to accentuate some of the most important properties of this material, among others the power of binding together various proportions of sand and other aggregates. The tensile strength, moreover, furnishes us with a knowledge of the behaviour of the cement under conditions which seldom or never come into play in actual work, and the stipulations respecting weight and fineness of grinding are somewhat loosely worded, in that they fail to indicate with sufficient precision the manner in which the weight is to be taken and the exact degree of fineness to be attained in the milling, which latter can only be shown by careful sieve-tests.

Weight Test liable to Considerable Errors.—The mode of filling

the bushel measure, which is one unnecessarily large for testing purposes, is a matter of great importance. This subject was brought under the attention of the Institution of Civil Engineers during the discussion on Mr. Grant's paper in 1865, by Sir F. J. Bramwell. He stated that "he knew by experience that when dealing with granulated matter, it was almost impossible, even with the greatest care, to get uniformity of conditions in the respective trials; that was to say, to get the same amount of granulated material into a particular measure. In corroboration of this he would state the results of what he had tried lately. A quantity of cement was poured into a bushel measure by a man accustomed to the work, and struck off level; it then weighed 107 lbs., exclusive of the weight of the measure. Then another portion of the same cement was poured slowly out of the sack down an inclined board into the bushel measure and it then weighed only 97 lbs.; he then had it shaken down in the measure and the weight then got up to 132 lbs."

Sir F. Bramwell proposed a Specific Gravity Test.—Sir F. Bramwell pointed out that "when it was found that with the same measure of capacity and the same material there could be a variation of from 97 lbs. to 132 lbs., he could not help thinking, if a test of gravity could be obtained which was not liable to these variations it would be a very desirable thing." He further stated that the weight test "should be combined with that of sifting," an axiom that subsequent enquirers have amply confirmed. He said that if this was not done, "the requirement as to weight was liable to act as a premium for coarse grinding." In confirmation of this assertion he adduced the following figures:—"He had sifted through a sieve of 900 holes to the square inch, a certain portion of the cement which weighed, as before stated, when very carefully put into the measure, 97 lbs., and when put in in the ordinary way 107 lbs. to the bushel; those portions which would not go through the sieve were then poured into the bushel measure with the same care as that which made the unsifted weight, as previously stated, only 97 lbs., with this care the coarse weighed as much as 101 lbs., and when shaken down hard into the measure 144 lbs., whereas the unsifted cement had weighed, as before stated, only 132 lbs. He then took by themselves the fine particles which had passed through the sieve and they then weighed only 98 lbs. (93?), as against 97 lbs., and when shaken down 130 lbs., as against 132 lbs. for the mixed, and 144 lbs. for the coarse."

From these experiments he was led to believe that with the weight test, in its present form, "there might and probably would be badly ground cement present in the mass."

Specific Gravity ascertained by Sir F. Abel.—From some further tests on this same cement made by Sir F. Abel at Woolwich, it was ascertained that the specific gravity was 3.11, equal to a weight of 249

lbs. per bushel, which would seem to show that if the cement could be obtained in a really solid form it would weigh 249 lbs. per bushel, the observed difference being solely due to the voids.

Specific Gravity Test not Suited for General Use.—This suggestion respecting a specific gravity test is a matter of considerable importance, and though this plan has received much attention from subsequent experimenters, it has never become popular, as it is rather too refined a test for actual practice, as Sir F. Bramwell himself, indeed, appeared to think.

The specific gravity test, moreover, has been shown to fail to indicate reliably the degree of calcination to which the cement has been subjected, and it certainly furnishes no guide as to the quality of the material. It has been pointed out by German chemists that Portland cement probably acquires its relatively high specific gravity before it is completely burnt; certainly before the stage of incipient fusion is attained, at which time, owing to the formation of a slag-like mass, we might have expected the molecules to be drawn together more closely, leading to an increase in density. We have given some figures relating to this test in the chapter on Cement Analysis, p. 90.

Form of Early Test-Briquettes.—All of the earlier tests under Mr. Grant were conducted, as we have seen, with briquettes having a sectional area at the point of fracture of $2\frac{1}{4}$ square inches. Mr. Reid in his work on cements* takes the credit for having suggested the pattern first used; this was avowedly copied from French specifications, which involved the use of a briquette of the shape shown in Fig. 47, the notch forming the neck to receive the clips being cut out by hand from a solid casting after the lapse of a prescribed period of time. This must have been a somewhat clumsy plan, necessitating considerable waste of time and money, and it was, moreover, very liable, we should think, to lead to erroneous results in the tests, due to injury to the briquette during the cutting process. The French tests, on a sectional area of $2\frac{1}{4}$ square inches, were of course based upon English measurements for the benefit of manufacturers in this country who at that period were alone able to supply the cement.

Proposal to increase the Sectional Area of Test-Briquette.—At the time of reading his first paper on the subject in 1865, Mr. Grant was of the opinion that it would be advisable to modify the shape of the test-briquette and to increase the area at the point of fracture to 2 inches $\times$ 2 inches = 4 square inches, the new form of briquette proposed for this purpose being shown in Fig. 48, with shackles made to fit the same. This new shape was, however, speedily abandoned in favour of

* *The Science and Art of the Manufacture of Portland Cement*, . . . by Henry Reid, C.E. London, 1877. 8vo.

that shown in Fig. 49. It will be seen that the clip in this case passes through an aperture in the solid ends of the briquette, small castings being inserted in each aperture so as to provide a knife-edge bearing for the shackles to strain against. These frequent changes of form, and the many efforts made to obtain reliable results in the early history of cement testing, are extremely interesting.

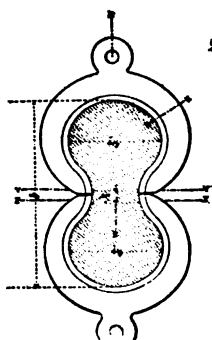


Fig. 48.
Briquette with Sectional Area at Breaking
Point of 4 square inches.

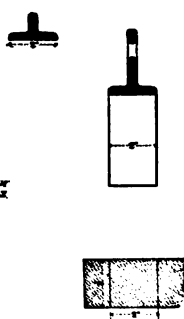


Fig. 49.
Modified Arrangement for Testing
Briquettes.

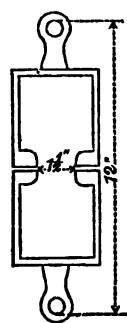


Fig. 50.
Improved
Pattern of
Briquette.

Influence of the Form of Briquette on the Tensile Strength.— In his second paper on the strength of cement, dated April, 1871, Mr. Grant gives a valuable table which we here reproduce, showing the results obtained by the use of the various forms of briquettes employed prior to 1866. It will be seen that ten different patterns were tried, the best results being obtained with Nos. 2 and 3, and it was, therefore, decided to employ briquettes of the former of these shapes for all future experiments. Many of these patterns were tried in order to discover the best mode of avoiding any distortion or departure from the line of strain. The plan originally adopted with this object was that shown in Fig. 48, subsequently altered as seen in Fig. 49. It was found, however, that this modified arrangement frequently broke at the holes at each end, instead of at the neck, and it was in the attempt to avoid accidents of this kind that knife edges were inserted in the eye and pin at each end. The fiddle-shaped mould, No. 10 in table, did not break uniformly at the neck, the slightest distortion causing it to break obliquely in a diagonal line. Distortions and irregular strains were often caused by the slipping of the clips, or by the tendency of certain of the clips to open when the strain was applied, and in order to obviate this the clips were strengthened. The form first used with the sharp angles, shown in Fig. 47, often broke very irregularly owing to imperfections in the bearing surface of the clips, and this evil was reduced

to a minimum by rounding off the edges, as seen in the improved pattern, Fig. 50.

RESULTS OF EXPERIMENTS ON DIFFERENT FORMS OF MOULDS. WEIGHT OF PORTLAND CEMENT USED, 114 LBS. PER BUSHEL. OCTOBER AND NOVEMBER, 1866.

No.	Form.	Dimensions at Breaking Point.	AT 7 DAYS.			AT 30 DAYS.		
			Breaking Weight.	Breaking Weight per Square Inch.	Average per Square Inch.	Breaking Weight.	Breaking Weight per Square Inch.	Average per Square Inch.
1		1½" x 1½"	Lbs. 778·1	Lbs. 345·8	Lbs. ...	Lbs. 1010·7	Lbs. 449·2	Lbs.
2		ditto	1034·7	459·9	...	1151·6	511·8	
3		ditto	1064·3	473·0	...	1145·4	509·0	
4		ditto	918·9	408·4	...	969·0	430·66	422
5		ditto	924·0	410·6	...	967·0	429·8	
6		ditto	860·0	382·2	...	912·1	405·4	
7		2" x 2"	1199·2	300·0	297	1354·7	338·7	337
8		ditto	1172·6	293·0		1315·1	328·8	
9		ditto	1190·5	297·6		1371·2	342·8	
10		ditto	1286·3	321·6	...	1460·3	365·0	

New Shape of Briquette not a Success.—As will be evident from the table, none of the improved shapes tested about this time gave results that were fairly comparative with those obtained with the original pattern, and this form was ultimately adopted for all subsequent tests, comprehended in the series covered by Mr. Grant's earlier papers, but in reverting to the use of the original clips, knife edges were inserted in the eye and pin at each end.

Area of Briquette at Point of Fracture.—Following the precedent of the German experimenters, the size of the test-briquette in common use in this country has in recent years been reduced, and it is now customary to employ briquettes having a sectional area of only 1 square inch at the point of fracture. Mr. Grant in his paper on Portland cement, read before the Inst. of Civil Engineers in May, 1880, gave some excellent instructions for the testing of cement, which we herewith reproduce, because his long experience entitles him to speak authoritatively on this matter. He had by this time been converted to the value of the sand test and the use of small briquettes. The form employed by him in his later experiments is shown in Fig. 51.

Instructions for Preparation of Test-Briquettes.—The following were Mr. Grant's instructions for making the tests:—Take enough cement to make as many briquettes of either neat cement or of cement with sand, as may be required. For neat, about 3.20 lbs. of cement will be required to make ten briquettes of the smallest size of 1 inch sectional area, and 16 lbs. for ten of the larger size of 2.25 square inches area. About 1 lb. of cement and 3 lbs. of sand will make ten of the 1-inch briquettes. 500 grammes of cement, 1,500 grammes of sand, and 200 grammes of water will make ten of the German normal briquettes and allow for waste. For testing the cement in different sacks, casks, or bina, a sample may be taken from each and numbered. For experiments, or to get averages, the samples may be taken in equal quantities from each and mixed. The cement, unless it is going to be used at once, ought to be spread in a thin layer on a slate or piece of wood, and

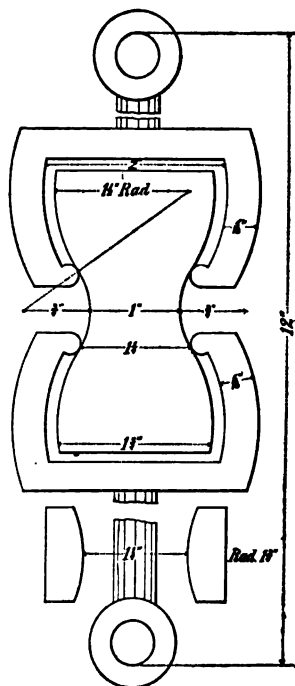
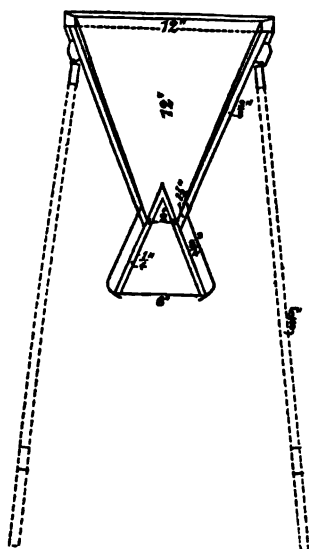


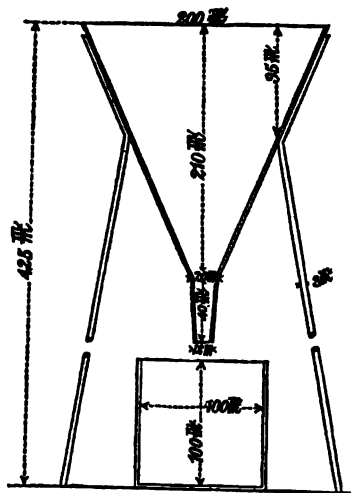
Fig. 51.—Briquette having Sectional Area of 1 square inch.

exposed to cool dry air as long as may be necessary. With newly-ground and quick-setting cements it is important to ascertain that they are fit for immediate use. Two cakes of neat cement 2 or 3 inches in diameter, about $\frac{1}{4}$ inch thick with thin edges, should be made, and the time noted in minutes that they take to set sufficiently to resist an impression of the finger-nail. One of these cakes, when hard enough, to be put into water and examined from day to day to see if it shows any tendency to "fly," by cracks of the slightest kind, beginning, and being widest at the edges. With slow-setting cement, however, cracks on the surface, beginning at the centre, are merely the result of the surface drying too rapidly from exposure to a draught or to external heat. The other cake to be kept in air and its colour observed. A small quantity,



BUSHEL.

Fig. 52.—Filler for Bushel Measure.



LITRE.

Fig. 53.—Filler for Litre Measure.

which may be 1, 5, or 10 lbs., or 10,000 grains = $1\frac{1}{2}$ lbs., to be sifted through the three sieves of 2,580, 5,806, and 32,257 meshes to the square inch, and the proportion by weight that will not pass through each sieve tested. The cement should be weighed, using a filler of either an imperial bushel measure; or a box of $\frac{1}{10}$ of a bushel capacity, which may be a cube of 6 inches by 6 inches by 6.16, or a cylinder of $6\frac{1}{2}$ inches diameter and 6.684 inches in depth (see Figs. 52 and 53). The weight to be taken in lbs. and decimal parts. Ten briquettes to be made with one part, by weight, of cement to three of sand which has been washed, dried, and passed through a sieve of 20 and caught on a sieve of 30 to the lineal inch. Twenty more briquettes may be made of neat

cement, to be tested as to strength after seven and twenty-eight days. The proportion of water (as of sand) to be to the cement by weight, viz., neat cement from 20 to 25 per cent. (or more) according to the fineness, the age or other conditions of the cement and the temperature of the air. With 3 parts of sand to 1 part of cement, 10 per cent. of the weight of the united cement and sand will, as a rule, serve. Sufficient water must be used to make a stiff paste, but no more. When cement is new or hot, lightly burnt, finely ground, or made up in hot weather, it takes more water, but a very little more than is sufficient to make it into a stiff paste will sensibly diminish the strength. With 3 parts of sand to 1 part of cement the quantity of water required hardly varies from 10 per cent. A number of pieces of wet blotting-paper, a little larger than the mould, one for each mould, may be laid on the slate or marble bench, and the moulds put upon them. The moulds are filled with a small trowel, and the briquettes made with the spatula (see Fig. 55), the mortar being beaten till all the air has been driven out and the mortar has become elastic. The surplus is cut off level, and the surface left smooth. Dr. Michaelis, of Berlin, recommends another system of making briquettes of neat cement, which, however, is not adapted for very quick-setting cements, nor for briquettes made with a mixture of sand. It is known as the gypsum-plate process. The cement is mixed with from 30 to 35 per cent. of water, and poured into moulds resting on sheets of wet blotting-paper laid upon plates of plaster of Paris. The moulds are tapped or shaken. About 50 per cent. of the water is quickly absorbed, and, if necessary, more of the cement is added. The surface having been smoothed with a trowel or knife, the briquettes are dexterously dropped out of the mould. This process is a very quick one, and Dr. Michaelis claims for it that it leaves only the amount of water which is required by the cement for setting properly, and that greater uniformity is attained than by any other process. The briquettes can thus be made denser, taking more cement, and breaking frequently under a strain about 50 per cent. higher, or even more. The absorbent slab, he compares to the brick or stone with which mortar is in practice used. But to make strong work with cement it is necessary to soak with water bricks or stone before using them. No doubt, by long practice any one may produce uniform results by following this or any other process; but we have not succeeded in getting greater uniformity by this than we have by the process first described. When the moulds have been filled the briquettes are numbered, laid aside, and covered with a damp cloth till they have set sufficiently to be taken out of the moulds. The briquettes are then put on sheets of glass, or on slates, and laid in a flat box, having a cover lined with several layers of linen, woollen, or cotton cloth, kept damp. In this box they are kept until they have hardened

sufficiently to be put into water. This will vary from one or two hours to a day or more; but for uniformity, unless in cases of specially slow-setting cement, briquettes of neat cement may be kept for twenty-four hours, and those with sand for forty-eight hours, before being transferred from this box to the shallow tanks in which they are to remain till the moment of testing. The numbers on the neat cement briquettes may be made with a sharp point or with a strong pencil. For the sand and cement briquettes, numbers previously written or stamped on small pieces of zinc will be found more convenient. The water and the testing room should be kept at a temperature as nearly uniform as possible, say, from 60° to 70° Fahrenheit; but if the box and tanks, in which the briquettes are kept, be covered, moderate changes of temperature will not materially affect the results.

It may be useful, especially at certain seasons, or in countries in which the temperature varies very much, to note the readings of the maximum and minimum thermometers. Seven, twenty-eight, or more days after the briquettes have been made, their tensile strength can be ascertained. In doing this as much uniformity as possible is to be observed in applying the weight slowly and gradually, avoiding all sudden jerks. The result for each briquette being recorded, the average is ascertained.

The test with neat cement at the end of seven days is of little more use than to show approximately, by comparison with the tests made at a later date, whether the cement has increased in strength. The later tests are of most value, and especially those made with sand.

Appliances for Testing.—The apparatus and appliances which it is necessary or desirable to have for making tests and experiments are: a number of boxes about 4 inches deep, lined with lead or zinc, having loose covers and a tap for drawing off the water; a similar box, which need not be lined, but the lid of which should be covered inside with several layers of coarse linen, woollen, or cotton cloth, to be kept always damp, and made to fit closely over the box; a number of pieces of plate-glass or slates about 12 inches by 6 inches, or 15 inches by 8 inches; an imperial bushel measure; a measure of one-tenth of a bushel, either 6 inches square by 6.16 inches deep; or, if cylindrical, 6.5 inches in diameter by 6.684 inches deep; scales for weighing a bushel or smaller quantities of cement, sand, or water; weights of various denominations, including a pound and decimal parts of a pound; 10,000 grains and decimal parts; funnels or fillers for the bushel and smaller measures (see Figs. 52 and 53); brass wire sieves of 400, 900, 2,580, 5,806, and 32,257 per square inch (the first two are used for sand, the last three for cement, and correspond with the sieves used in Germany of 400, 900, and 5,000 per square centimetre); ten or more gun-metal moulds for

making briquettes of 1 square inch sectional area (Fig. 51), and, if required, similar moulds for briquettes $1\frac{1}{2}$ inches by $1\frac{1}{2}$ inches = 2.25 square inches; machine for ascertaining tensile strain (see Fig. 58, p. 225); a spatula (Fig. 55), with thin edges to the blade, weighing $7\frac{1}{4}$ ozs., to be used for beating the cement and sand in the moulds; straight-edges for striking off the measures; a straight-bladed knife for cutting off surplus cement in making briquettes; one or two small trowels; two strong basins or mortars; maximum and minimum thermometers; blotting-paper; a graduated glass for water; sand, washed, dried, and sifted through a 20, and caught on a 30 meshes to the inch sieve = 400 and 900 per square inch, and forms for tabulating and registering results.

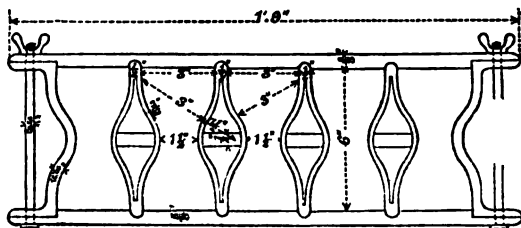


Fig. 54.—Frame for Moulding Five 1-inch Briquettes.

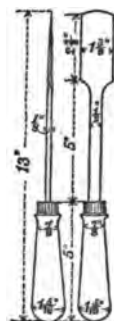


Fig. 55.—Spatula for Cement Testing.

Professor Unwin on Cement Testing.—Professor Unwin, in the course of a paper contributed to the *Journal of the Society of Chemical Industry* in April, 1886, on this subject, points out that “testing began with comparatively crude tests of the tenacity of briquettes or test-pieces of neat cement, which at first were made of an excessively bad form, and were seldom tested after more than seven days’ hardening.” He proceeds to show that the defects of this plan soon became evident, and caused great differences in the apparent strength of the same quality of cement, in accordance with the amount of water used in gauging, the pressure employed in moulding, and so on.

Tensile Strength of Briquette depends to some Extent on the Form.—Many different shapes were, as we have seen, employed, and at one time engineers vied with one another in the invention of new patterns for the briquettes. As Professor Unwin says, “the influence of the form of the briquette on the strength is considerable,” different briquettes of the same cement moulded in different forms gave results at seven days, ranging from 280 lbs. per square inch to 460 lbs. on the same area. This question was, as already stated, carefully investigated by Mr. Grant. Even now, when engineers are fully informed of the

importance of the shape of the briquette and of the wide range in values arising from trifling variations in the manipulation of the material during the process of moulding the blocks, we are, at any rate in this country, still very far from the possession of any such generally accepted system of conducting the testing process, as shall ensure uniformity in the results. Indeed so many discrepancies in the procedure are to be found that it is exceedingly difficult to get absolutely trustworthy comparative tests. Professor Unwin refers to the care and skill with which cements are examined in the German State laboratories, and it must be remembered that, in many parts of the Continent, cement producers and cement users have combined to enforce the adoption of a uniform system of tests.

Present Method of Testing Cements.—Cements are now generally tested, either alone, or mixed with certain proportions of sand, the latter tests being by far the most scientific and searching. We must remember, moreover, that cement is tested for two entirely different motives:—

1. To ascertain whether it satisfies certain contract conditions and complies with definite standards laid down in the specification. For these tests the element of time is an important consideration.

2. For scientific purposes, to determine its properties, its value as a constructive material, and the best methods of employing it.

Engineering Tests of Cement.—Under these latter tests the engineer has, as far as possible, to reproduce the exact conditions and surroundings to which the material will be exposed in practice, and his investigations must necessarily be continued for more or less considerable periods of time. He must assure himself by protracted tests that the cement is a binding agent that may be relied upon for all reasonable periods. The classes of tests which satisfy the first of these requirements are from the very nature of them imperfect and unsatisfactory, and incalculable injury has been inflicted upon cement users in the past, because every effort was made to produce materials capable of giving the best results under these commercial tests, and over-limed coarsely ground cements were preferred to those which, under a more scientific system of testing, would have established their undoubted superiority. In this connection Professor Unwin declares that "the great progress of the cement manufacture in Germany, and the production there of cements stronger in test and of more value in the market than English cements, is to be traced directly to the adoption of more rational tests."

Fallacies in the Method of Testing.—A cement employed constructively is only in a very few exceptional cases used in tension, but all our English tests would seek to establish its quality by its power of resisting tensile strain. We never, except as a stucco, use Portland cement neat, but it is by the examination of a briquette of neat cement

that we too often seek to ascertain its quality. We invariably allow an interval of weeks or months to elapse before we submit our brickwork or masonry to severe stress, but our judgment is in most cases pronounced upon a sample of cement by its behaviour after a seven or at most a twenty-eight days' test. Our walls and buildings have to stand the strain of exposure to sunshine and shower, to heat and cold, and to every change in the weather, but our cement-tests are carefully kept at one even temperature in a "water-bath."

Conditions under which Cement is Actually Employed.—As Professor Unwin remarks, "obviously the ordinary tests are empirical, and may be misleading. Almost every circumstance which markedly affects the strength of a small briquette, tested neat and soon after setting, produces a less effect on the strength of a mass, mixed with other materials, and tested after a longer interval of time."

Qualities needful in a Cement.—He proceeds to show that "the constructional value of a building cement depends on two quite distinct elements—on its power of setting into a rigid form soon after it is gauged, and on its power of attaining in course of time a considerable strength." We may take it for granted that no manufacturer of Portland cement at the present time would think of sending out a material incapable of satisfying the former of these requirements, though we must admit that hot over-limed cements are still occasionally met with which will set well enough for a day or two, but eventually go abroad even in the short space of the seven days' test. Such cases are, however, rare.

The Induration of Cement takes place according to a Uniform Law.—When ample time can be devoted to the study of the quality of any given sample of cement, and when we can note its behaviour through a long series of months or years, we shall find, as Prof. Unwin has remarked, that "beyond the first week, and up to the period at which the full strength of the cement is reached, the rate of hardening follows approximately a very simple law." The factors may be arranged in the form of a readily intelligible formula, the constants of which clearly indicate the character of the cement.

"Let x be the number of weeks during which a test-piece has been hardening. Then the strength y in lbs. per square inch at that age is given very approximately by the equation—

$$y = a + b(x - 1)^n$$

where a is the strength at seven days, and b and n are constants depending on the rate of gain of strength with age.

"For all tension tests of Portland, n may be taken as one-third. For ordinary limes it has a larger value. For compression tests of

comparatively large blocks of Portland, n is one second; consequently, two tests of a cement at different ages determine the remaining constants of the formula."

The Professor states that the curve given by this formula reconciles the anomalies which must always occur in tensile tests, and produces an average of the somewhat discordant results. He finds by its application that neat cement tests attain their full strength in three or at most four months, while sand tests increase regularly in strength for two or three years. On working out the results from a long series of tests by Mr. Grant, he obtained for neat cement and cement mortar (1c. + 3s) the following results:—

TESTS OF BRIQUETTES OF NEAT CEMENT AND 1 CEMENT TO 3 SAND AT DIFFERENT AGES OF HARDENING IN POUNDS PER SQUARE INCH.

AGE IN WEEKS.	NEAT CEMENT.		1 CEMENT TO 3 SAND.	
	Observed.	Calculated.	Observed.	Calculated.
1	363	363	157	157
4	415	431	202	214
13	470	471	244	249
26	525	500	285	274
39	512	521	307	292
52	517	543	320	305
104	590	589	351	345
156	585	...	350	372

Specific Use of Prof. Unwin's Formula.—In the foregoing table the value of a in the case of the neat cement is of course 363, and in the case of the sand mixture 157: the complete formula being—

$$\left. \begin{array}{l} \text{Neat} \\ \text{Cement,} \end{array} \right\} y = 363 + 48 \sqrt[3]{x - 1}.$$

$$\left. \begin{array}{l} 3 - 1 \\ \text{Mortar,} \end{array} \right\} y = 157 + 40 \sqrt[3]{x - 1}.$$

In the graphic diagram for these two substances, on the next page, the actual tests are indicated by dots, the calculated curve is shown by the bold line.

By the application of this same method in the case of coarse and fine grinding, and for various qualities of sand, Prof. Unwin shows how the formula is affected by each different set of conditions. There is no doubt that for careful and comparative tests of cement the application of the graphic method is of great importance, and we commend to all who are interested in cement tests this very valuable and thoughtful essay.

No Definite Limit can be Assigned for the Period of Induration.—It is impossible to assign a fixed limit to the duration of the period within which neat Portland cement may continue to increase in strength. Some cements appear to show a slight increase in this respect up to five or six years, but these cases are exceptional, and in most dense well-made cements the induration has reached its maximum in under two years. After this period the briquettes in certain cases fall back slightly in tensile strength, as if some physical change took place in the structure or arrangement of the particles. Such decrease rarely exceeds 10 to 15 per cent. of the maximum strength.

Value of Long-extended Tests.—It is interesting and valuable to possess records of such protracted tests, and to know the exact composition of the cements with which they were carried out, as it is only by

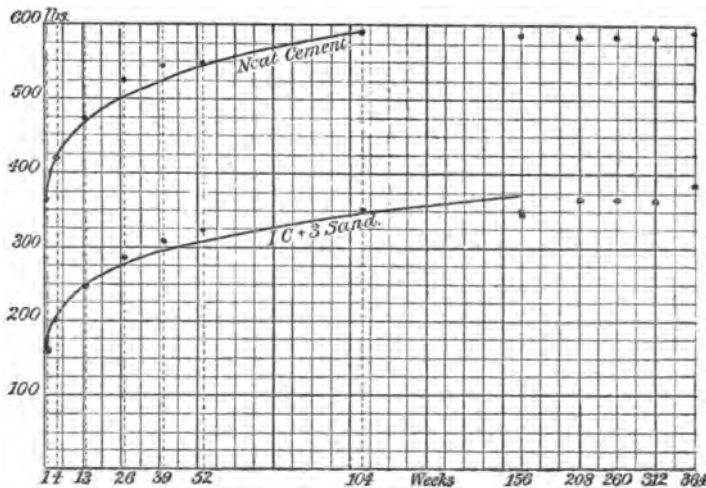


Fig. 56.—Tensile Strength of Cement and Cement and Sand Mortar.

the tabulation of numerous experiments and the comparison of a large number of analyses that we can hope to acquire any accurate knowledge of the somewhat obscure changes which are slowly effected in the course of induration.

Series of Tests of Warwickshire Cement.—We might multiply examples to show this process of “going back” from previous works on cement, but we prefer to adduce a few original and reliable tests to illustrate our meaning. The following experiments exemplify this process in a very remarkable way. They were carried out by one of the authors with some Warwickshire cement in 1888.

The sample in question was burnt extremely hard, and was of a dark blue colour. It was ground so that it all passed a 50 × 50 mesh sieve.

CALCAREOUS CEMENTS.

CHEMICAL ANALYSIS.

Insoluble residue,	4.557
Silica,	16.865
Ferric oxide,	4.831
Alumina,	6.360
Manganese oxide,	trace.
Lime,	62.507
Magnesia,	2.365
Sulphuric acid,	1.589
Potash,	.976
Soda,	.527
Total,	<u>100.577</u>

TESTS OF THE ABOVE CEMENT.

Neat cement, water 16 per cent. The mixture set slowly.

7 days.	28 days.	90 days.	550 days.
Lbs.	Lbs.	Lbs.	Lbs.
515	630	710	695
500	630	760	670
600	620	730	685
660	650	800	660
650	650	780	655
630	660	750	685
620	570	760	660
650	600	790	655
615	620	750	705
690	620	815	675
Average of 10 tests.			
613	625	764.5	674.5

Cement 1 part, standard (Leighton Buzzard) sand 3 parts by weight, water 10 per cent.

7 days.	28 days.	90 days.	550 days.
Lbs.	Lbs.	Lbs.	Lbs.
185	205	220	310
200	210	215	290
200	220	200	305
200	215	205	335
195	200	215	300
210	215	205	295
200	225	230	300
210	205	200	240
195	225	215	325
200	205	240	325
Averages.			
199.5	212.5	214.5	302.5

Critical Period during Induration.—In the above tests it will be observed that the values for the neat cement indicate a decided falling off between the 90 days' test and that at 550 days, and all observers

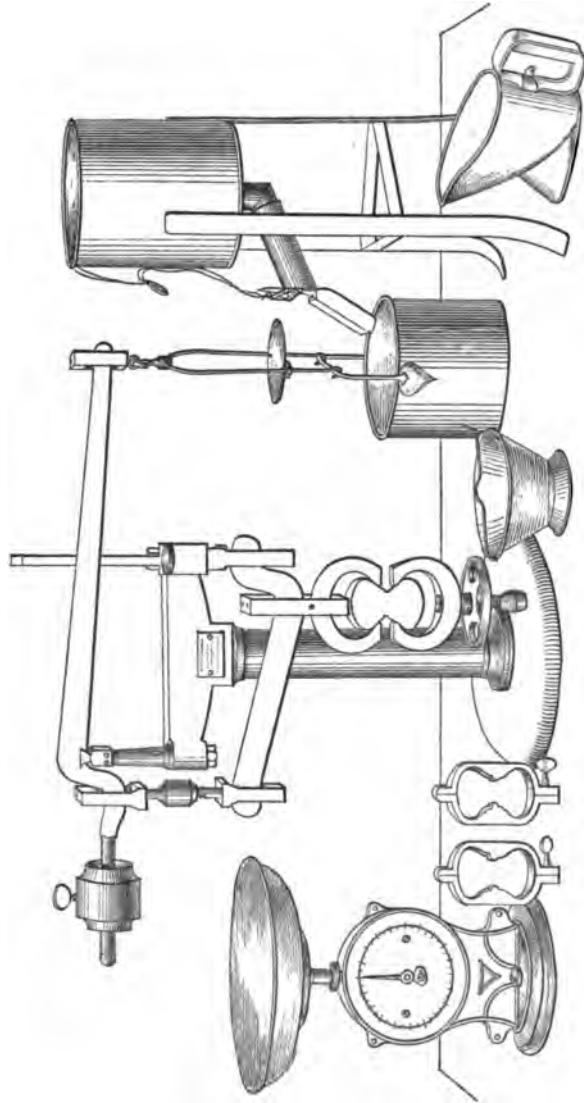


Fig. 57.—Standard Machine employed in Germany and Austria for Testing Cements.

who have carried out corresponding experiments will have noticed the intervention of such a critical period generally before the end of the second year, especially in very dense cements. No such decrease in

strength is apparent in the sand tests, and it is probable that some molecular changes occur during the induration which are not yet understood. This critical period does not always occur after the same interval, and it varies in accordance with the composition of the cement, the temperature at which it has been fired, and the degree of density that it has attained. A well-known writer on Portland cement has attempted to explain away this falling off in strength and to attribute it solely to carelessness in testing. He even says concerning some breaking weights which indicate just such a diminished strength—"It is to be hoped that no more of these records of questionable value will be published, for their misleading and uncertain character has already created too much scepticism on the possibility of cement improving in value."

German System of Cement Testing.—We have referred more than once to the German system of testing, and we give in the case of slag cement a translation of an official report on a series of experiments conducted with that material. In Appendix C will be found a full translation of the Regulations under which such standard tests are conducted. We herewith reproduce an illustration of the testing appliances used in Germany and Austria for these official tests (see Fig. 57).

The Adie Testing Machine.—One of the oldest and best-known cement testing machines in the market is that made by Mr. Patrick Adie, The Broadway, Westminster. It is used by many Government departments, and has long been considered the standard apparatus in this country. The maker states that his chief aim in the construction of his machines has been to secure the most accurate and undeniable results with absolute permanence and non-interference of the hand of the operator; thus, all springs and screws are dispensed with, and the simple steel lever, and vernier (with weight attached) travelling on rollers, is adopted. The vernier is caused to travel along the lever by means of a cord, passing over pulleys fixed to the standards, and thus all need of applying the hand to the lever during the progress of the test is avoided. In order to make this more unquestionable, in addition to the speed-reducing wheel and pinion, a patent automatic regulator can be added. As there are no compound levers, spring balances, or other appliances liable to give a multiplied error, or to be in any way uncertain in action or unreliable in results, this machine has everything in its favour, and compares well with other forms of testing apparatus. We illustrate the No. 2 machine of Adie (see Fig. 58), made with automatic regulator, but a somewhat simpler form of machine can also be supplied.

The Goreham Flourometer.—This is a simple piece of apparatus for separating from a sample of cement all the very finest particles (flour), and for estimating the relative proportions between fine and coarsely-ground material. In using the flourometer, a fixed quantity of the

cement to be tested is placed in a special receptacle, and air is forcibly driven through it, which causes the cement flour to separate from the residue. All those particles which are sufficiently light are carried through the upcast tube, and then sink to the bottom of the settling chamber. When all the flour has thus been expelled, the residue, which consists of the coarser particles, is weighed, and the difference between the weight of the residue and the weight of the entire sample indicates the amount of the flour, which latter can readily be expressed as a

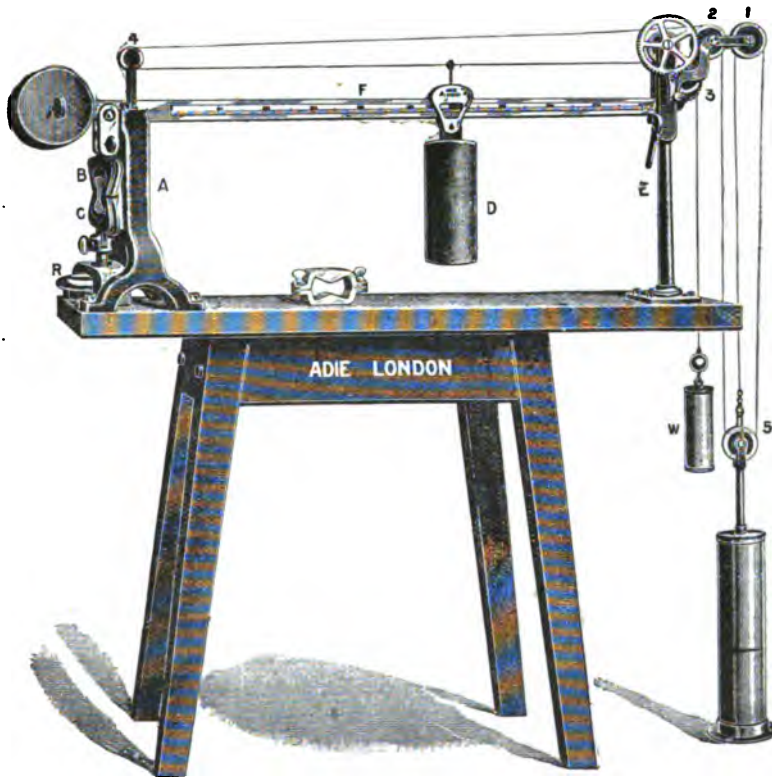


Fig. 58.—The Adie Testing Machine.

percentage of the whole amount. A good sample of cement should yield from 40 to 50 per cent. of flour by this test. The War Office authorities specify a minimum of 45 per cent. It is asserted that this test is much more reliable than the sieve-test, and that no cement which yields less than 42 per cent. of flour will show good results in practical work.

The apparatus consists of an aërometer for providing the necessary supply of air at any desired pressure, and the flourometer itself, with which the separation is effected. The weight of cement to be used for

each test (preferably 40 grammes) is placed in a glass vessel provided for the purpose, and the rubber tube connected with the aërometer is then attached. Each test requires about 45 minutes, and the inventor recommends that the resulting flour should be examined under the microscope, and also tested by rubbing it on a piece of glass with a palette knife, to see that it is not gritty. Unless care is exercised in carrying out the test, it is possible that all the flour may not be entirely removed from the sample, or that a little of the residue may be carried over into the settling chamber. This apparatus is, however, undoubtedly capable of furnishing useful and reliable information respecting the quality of cements.

Arnold's System of Cement Testing. — A method of testing cement, devised by Mr. Arnold, deserves passing mention, as it no doubt eliminates some of the imperfections in our present system which arise from the differences in handling which it is impossible altogether to avoid. It is well known that one man will get results some 10 or even 20 per cent. better than another with the same sample of cement. Mr. Arnold's method consists in filling the mould for the test briquette with a proper quantity by weight of the dry neat cement, which is then consolidated under a screw-press, resembling in construction an ordinary office copying-press. The plate on which the moulds rest has shallow sides, thus making it a bath. After removal from the press, each mould having been separately pressed, the bath is filled with water (when full it contains a depth of about $\frac{3}{8}$ of an inch), and the moulds stand therein for twenty minutes before removal. The moulds are made deeper than is required for the section of the briquette. Metal dies which exactly fit the mould are placed upon the top of the cement before it is inserted in the press, so that when the die is properly pressed down, its top is level with the top of the mould and no further compression can take place. Thus a uniformity of pressure is insured in the case of each briquette moulded from the same sample of cement. In order to avoid difference arising from varieties in the bulk of different qualities of cement, it is pointed out that dies of various thicknesses can be used. It is claimed for this system of making briquettes that much greater uniformity is attained than by the plastic method, that the services of an experienced man are not required, that the requisite amount of water and no more or no less is used, and that air bubbles are entirely avoided. The patentee states, moreover, that the evidence of a blowing cement will be noticed in 24 hours after moulding the briquette, and that owing to the absence of disturbance, after admixture with water, any particles of free lime present are invariably detected at the point of fracture.

CHAPTER XVI.

ACCELERATED TESTS FOR CONSTANCY OF VOLUME.

CONTENTS.—Reasons for such Tests—The Origin of the Boiling Test—Tests by Tetmajer — Maclay — Erdmenger — Prüssing — Heintzel — Fajja — Results obtained by Accelerated Tests—Verdict in Germany and America as to the Value of these Tests.

Reasons for such Tests.—A desire has constantly been expressed by cement users from the earliest period when cement became subjected to regular tests, for some more rapid means of ascertaining the reliability of the material than the ordinary tensile tests carried out with suitable briquettes at fixed intervals spread over a considerable period of time. The announcement, therefore, of the discovery of a method of forming an opinion concerning any sample of cement in a few hours was hailed with satisfaction, and the new tests were widely accepted by engineers and manufacturers, without any very searching enquiry concerning their practical utility and value.

The Origin of the Boiling Test.—We owe the boiling test in its original form to Dr. Wm. Michaelis of Berlin, who, some thirteen or fourteen years ago, described a system of dealing with cement samples in the following way:—50 grammes of the material to be tested were made up with about 13 to 15 grammes of water to a paste of normal consistency, and thoroughly worked with the trowel for about one minute, to expel air-bubbles. The cement mortar was then spread in pats on glass plates, the pats were to be about 1 centimetre thick in the centre, and to be thinned out all round the edges in the usual way. The pats were allowed to set for 24 hours in a covered vessel in an atmosphere saturated with moisture or steam vapour. They were then introduced either while still on the glass plate or after being detached from it into a water-bath; the water was at first quite cold, and just sufficient water was used to cover the pats completely. The water was then slowly raised to the boiling point in about ten minutes, and maintained at boiling temperature for three hours, after which the pats were taken out and examined. If any extra water was needed to maintain the level in the water-bath, it was to be added in small quantities at a time, and as nearly at the boiling temperature as possible. A sound cement would stand this test without any sign of cracking, and become considerably harder for the boiling, while it was contended that a treacherous or unsound cement would either crack and fall to pieces in the bath or it would

go abroad (i.e., crumble) into mud. Sundry slight modifications in the procedure have been proposed. Thus, the sample pats were directed to be made up on moistened blotting-paper, placed on a glass plate, and allowed to set, after which the blotting-paper was removed and the tests were conducted as before.

Tetmajer's Test.—Professor Tetmajer advocated a very similar plan of conducting the experiment, only he employed the cement made up into little balls about 2 inches in diameter, and of such a consistency that they could be patted down on a glass plate and flattened out by the pressure of the hand into circular pats, free from cracks. The pats thus prepared were to be kept in a damp atmosphere for 24 hours and were then placed in a cold bath, which was brought up very slowly (in $1\frac{1}{2}$ hours) to the boiling point, and boiled for six hours continuously.

Macclay's Test.—Macclay proposed a modification of the Tetmajer test for use in America, and he employed four pats of neat cement, made up on glass plates with water into a very stiff consistency. These pats were to be about $\frac{1}{2}$ -inch thick and 3 inches in diameter. One of these pats was to be placed, directly it was made up, in a steam oven at 90° to 95° Centigrade. The second pat was to be placed in the oven when it had become set hard enough to resist penetration by a normal test-needle, loaded with a weight of 1 pound; while a third pat was to be allowed double the setting period indicated by the previous test before being introduced into the oven. The fourth pat was only placed in the steam oven after 24 hours. The four pats remained in the steam oven at the temperature indicated for three hours, and they were then placed in boiling water for 21 hours, when the test was complete. If the cement is very defective owing to excess of free lime, improper burning, or other causes, the trouble generally shows itself in the cracking or distortion of all four pats. When the cement is not so bad, the cracking and swelling takes place in the first three pats only, and when the cement is still less defective only the first two pats crack or swell. Failure in No. 1 pat can, as a rule, be disregarded. For the United States Army Department tests the boiling is to last for six hours.

Erdmenger's Test.—Dr. Erdmenger was in favour of an even more severe test than simple boiling, and he has arranged a special apparatus in which the samples of cement can be boiled under a pressure up to 40 atmospheres. Dr. Michaelis has also designed a similar apparatus for subjecting samples of cement to boiling under pressure, and he recommends that the test should be conducted at 450 lbs. per square inch. Certain interesting results with respect to the induration of cements have been studied under these very severe conditions, but it can scarcely be maintained that tests of this rigid kind should be imposed upon

all cements, for many materials which have been found to give excellent results in practice have failed entirely under these onerous conditions.

Prussing's Test.—Some of the special accelerated tests involve the treatment of cement by processes which would appear to be very unfair to this material from the point of view of chemical action and the generally-accepted theories of induration. Thus Prüssing advocates that 100 grammes of cement should be made up into a paste with from 5 to 8 per cent. of water, in accordance with the fineness of the grinding, and very intimately mixed; indeed, he specifies rubbing the mixture through a sieve having 120 meshes to the square centimetre, after which it is to be spread uniformly into a mould and stamped into a cake in a press at 50 atmospheres pressure. Two such cakes, directly they are taken out of the moulds, are laid on a glass plate, and are placed in a box where they are protected from evaporation. They remain for 24 hours to become set, and are then transferred to a vessel of cold water. One of the cakes remains under water for 28 days to indurate, and the other is taken out in two hours' time, and, if it is uninjured, it is placed in a water-bath at a temperature of from 90° to 100° C. If, after remaining four hours at this temperature, the pat is still uninjured and free from cracks, the cement may be pronounced safe under all ordinary circumstances, but it is usual to let it remain for twenty hours longer in the water-bath at the boiling point. It is to be regarded as entirely reliable and especially sound and good if it stands this treatment.

The Heat Test of Heintzel.—Certain of the tests appear to be somewhat whimsical and fantastic. Among these we may mention the red-heat test, under which a ball about 5 centimetres in diameter, formed of neat cement, is moulded in the hand, and the quantity of water necessary, which may be about 20 per cent. of the weight of the cement, is found to be that which will slightly soil the hand, but will leave the ball capable of being pressed into shape while being handled. With quick-setting cements rather more water is needed; thus, taking 300 grammes of cement, up to 62 or 63 cubic centimetres of water may be employed with advantage. The ball, when ready, is laid on a plaster of Paris slab for about five minutes, or so long that it will no longer readily mark with the finger-nail, and it is then placed on a thin iron plate or on a wire triangle, and is supported over the flame of a Bunsen burner. The point of the flame must at first be kept well below the test, for if heat is applied too rapidly, little splinters, due to the steam evolved by the moisture in the ball, will be thrown off. As the ball dries, the flame is brought nearer and nearer, until it entirely surrounds the ball, and this may take place in about half an hour. During the second half hour the bottom of the ball attains a dull red heat, and a plate of cold glass held above it ceases to show any condensation due to

escaping moisture. The test is then complete, and if the ball remains sound, the cement may be pronounced to be of excellent quality. This very stringent test was devised by Heintzel, but it has never been very widely employed.

There are several varieties of these tests, some of them requiring considerable skill in conducting them, and this would therefore render them rather unsuitable for uniform tests.

Faija's Test.—Several forms of the hot-water test have been carried out in this country, but perhaps that of Mr. Faija is most widely known. It is based on the principle that moist heat accelerates the setting of cement; and it is asserted with some good show of probability that boiling means seasoning, and that a few hours in the water-bath at the boiling point are equivalent to as many days in damp air under ordinary conditions. The apparatus for conducting the test consists of a covered vessel in which water is maintained at an even temperature of from 110° to 115° F.; the space above the water is therefore filled with the vapour rising therefrom, and is at a temperature of about 100°. Immediately the pat is gauged, it should be placed on the rack in the upper part of the vessel, and in five or six hours it may be placed in the warm water and left therein for nineteen or twenty hours. If, at the end of that period, the pat is still fast to the glass, or shows no signs of blowing, the cement may be considered perfectly sound; should, however, any signs of blowing appear, the cement should be laid out in a thin layer for a day or two, and a second pat made and treated in the same manner, as the blowing tendency may only be due to the extreme newness of the cement.

Practical Results of Accelerated Tests.—As the result of the methods under which these accelerated tests are conducted, it is generally assumed that their effect is to indicate constancy of volume or "soundness," but it will readily be perceived that this does not necessarily follow. Many samples of cement which are found to give excellent results in practice, when made up with sand in the usual way, are reduced to mud, and lose all traces of cohesion under the boiling test. It must be remembered that all these heat tests expose the sample of cement to highly artificial conditions, and to such as would certainly not be found in the natural use of the material. They are in fact, many of them, so radically different from the conditions experienced by mortars or concretes in ordinary engineering practice, that it is safe to say that the results they yield can only be regarded with considerable suspicion. All the circumstances, moreover, which tend to accelerate the chemical and physical processes of induration in the natural use of the material, can hardly fail to be distorted and interfered with by the application of rapid heat and the employment of the boiling process. In an ideal system of acceleration, the aim should be to make use of procedures which differ as

little as possible from the circumstances attending the use of cement in the usual methods of engineering practice. It is hardly possible to conceive that the heat test, for instance, of Heintzel could prove otherwise than injurious to a slow-setting cement; and, if the induration of a cement is to any extent due to a process of crystallisation, prolonged boiling would certainly be most inimical to a satisfactory issue.

Verdict in Germany.—The German Union of Cement Manufacturers, when these tests were introduced, took measures, by the appointment of a Commission, to ascertain how far the practical results of employing cements in construction coincided with the verdict of the laboratory and the outcome of the accelerated tests. From an excellent report by Mr. Gary, who represented the laboratory in the work of the above Commission, we gather the following facts:—

Cements, none of which would pass the boiling test, were procured from ten different manufacturers in various parts of Germany under conditions affording entire secrecy. As soon as they were received they were submitted to tests in three different laboratories, and portions of each were also used in the preparation of cement wares, to be exposed to the weather.

Though the figures representing the laboratory results varied somewhat considerably under the hands of the several experimenters, the general results were easily reconcilable, and were upon the whole satisfactory, while the practical examples from the workshop, consisting of medallions, rosettes, and pipe caps moulded in cement, with the exception of a few unimportant cracks round the rims, set hard and stood well under exposure to the weather. Apart from the fine hair cracks, all the objects, after more than two years' hardening, were pronounced "still sharp cut and in good condition."

American Account of Accelerated Tests.—A writer in the *Engineering Record* draws the following final conclusions from the above report:—"The result of the investigation may, therefore, be summed up as determining that not one of the so-called accelerated tests for constancy of volume is adapted to furnish a reliable and quick judgment in all cases concerning the practical applicability of a cement. The investigation has further proved that all the cements which withstood the pat test in the normal system of testing are practically constant in volume when used in test-pieces and in cement wares. The increase in strength of the test-pieces with water- and air-hardening speaks well for the practical utility of the cements.

"The assertion quoted early in the report that the normal or standard tests were insufficient, particularly when the cement is to be hardened in the air in its practical application, has received no confirmation by the investigation of the Commission."

CHAPTER XVII.

THE EMPLOYMENT OF SLAGS FOR CEMENT MAKING.

CONTENTS.—Slags used for Adulteration—Dr. Michaelis on Slag Mixture—Composition of Blast Furnace Slags—Uniformity in Composition of Slag—Slag Cement as a Kiln Product—Production of Slag Cement—Passow's Process—Bosse & Wolters' Process—Snelus' Process—Necessity of Fine Grinding—Properties of Slag Cement—Storage—Chemistry of Slag Cement—Other Considerations Involved—German Tests of Slag Cements.

Slags sometimes used for Adulteration.—The days have now gone by, we may hope, when slags of all kinds are regarded with suspicion by cement users, owing to their occasional employment for the adulteration of Portland cement. It cannot be denied that for this purpose certain varieties of iron slag were extremely well adapted, since they approximate so closely in colour, weight, and composition to the cement itself that their presence could be detected only with difficulty, even by means of delicate chemical tests.

Nature of Slags used to mix with Cement.—The slags used for fraudulent additions to cement were generally those which had a tendency to disintegrate on exposure to the atmosphere, and which go abroad—i.e., crumble—naturally into a bulky gray powder, having at times an astonishing resemblance to Portland cement. The fact of this spontaneous disintegration would seem to argue that some change, either of a physical or chemical nature, took place in consequence of atmospheric action; probably these varieties of basic slag were selected chiefly because a powder could be obtained from them by mere sifting, without the expense and trouble of grinding, which is no easy matter in the case of the dense inert slags.

Dr. Michaelis on Slag Mixtures.—It is necessary that we should here allude to the opinions of Dr. Michaelis with respect to these admixtures of slag, for he has proved that with selected slags, used even in such large quantities as 30 per cent., it is possible to add considerably to the tensile strength of cement, both when tested neat and with the usual quantity of normal sand. He has, in his open letter of 1884, claimed that it is to the advantage, both of the user and of the manufacturer, that these mixtures should be permitted.

Some Slags unacted upon by Moisture or by the Atmosphere.—Certain varieties of acid slag would seem to be very little affected by air or moisture, and remain for years on the spoil-banks with arises as sharp and clean as they were upon the day when they were tipped. Doubtless it was the apparent inertness of these materials which led experimenters to form the opinion that it was impossible to use them in cement-making, for the great similarity in composition of some descriptions of blast furnace slag with the clinker of Portland cement must have frequently caused attention to be directed to this material, in order to find a possible use for it as a cement component.

Slags Produced at Extreme Temperatures.—It must here be remembered, however, that the temperature at which slag is produced is greatly in excess of that needed to prepare Portland cement clinker, and, moreover, that in the case of the clinker too high a temperature in the kiln, resulting in complete fusion of the mass, leads to the formation of a blue-black glassy substance (slag), which, in consequence of its vitrification, is of little practical use for cement. The analogy of the two processes would again deter the investigator from further attempts to employ slag in cement-making.

Admixture with Lime in Blast Furnace.—Certain inventors have not been deterred by the high temperature of the blast furnace, and have attempted to prepare a suitable slag by the use of such proportions of limestone as would produce a slag having a composition resembling that of cement clinker in the furnace itself. It was found, however, on actual trial, that with these high percentages of lime the heat was not sufficient to effect complete fusion, and the smelting of the iron ore was imperfect. It is essential for fluxing purposes that the slag produced should be extremely fusible. This proposed combination of cement manufacture with iron production was therefore abandoned.

Composition of Blast-furnace Slags.—A glance at the annexed table will show that many iron slags contain all the essential ingredients of Portland cement, though in none of them are they present in the same proportions as those selected by the cement maker. In almost every case there is a marked deficiency of lime, and nearly all the attempts made to utilise slag have involved the addition of lime in some form or other to the slag in a finely-divided state.

ANALYSES OF VARIOUS SLAGS * FROM IRON WORKS.

Locality.	Silica.	Alumina.	Lime.	Iron, Alkalies, Sulphur, &c.
1. Staffordshire,	41·99	23·27	31·62	3·21
2. South Wales,	42·84	28·84	26·13	2·11
3. "	32·30	15·70	44·80	7·20
4. Yorkshire,	39·47	23·66	32·12	4·75
5. Lancashire,	33·49	10·12	46·97	8·54
6. Staffordshire,	49·05	10·84	34·33	5·78
7. Warwickshire,	41·30	16·20	40·80	2·70
8. "	36·30	13·86	30·49	9·76
9. Scotland,	32·10	24·28	35·43	8·10
10. Nottinghamshire,	32·18	31·50	33·05	3·27
11. Lancashire,	38·68	13·13	45·82	2·37
12. Cumberland,	34·00	15·10	47·20	3·70
13. Derbyshire,	39·24	23·04	32·06	5·66
14. "	40·00	11·50	40·60	7·90
15. Lincolnshire,	32·86	21·88	40·34	6·12
16. "	31·37	19·69	40·23	8·71
17. Northamptonshire,	39·06	21·54	37·16	2·24
18. North Wales,	31·28	12·41	46·10	10·21
19. Newcastle,	26·37	14·42	48·84	10·07
20. "	34·15	16·68	43·39	5·78
21. "	31·05	23·15	36·51	9·29
22. Cleveland,	32·15	17·53	45·50	4·82
23. "	35·45	21·55	33·70	9·30
24. "	29·89	26·13	34·35	8·63
25. "	30·98	28·03	33·33	7·60

Uniformity in Composition of Slag.—The quality of the slag produced at any one works, where the same description of iron is being manufactured from ore of uniform type, varies within very narrow limits, as will be seen from the appended table, which gives the average analyses of a series of years expressed in percentages of the chief constituents :—

	1888 to 1890.	1893.	1895.	1899.
Silica,	35·20	34·50	34·23	35·40
Alumina,	10·02	10·90	10·28	10·45
Ferric oxide,	0·21	0·18	0·33	} 0·91
Ferrous oxide,	0·55	0·64	0·64	
Manganous oxide,	0·30	0·46	trace.	
Calcium oxide,	47·10	47·44	48·26	46·74
Sulphate of lime,	1·56	1·44	1·87	1·72
Sulphite of lime,	2·17	1·99	2·07	1·81
Magnesia,	1·20	1·36	1·13	1·20
Alkalies (not determined),	...	...	...	...
	98·31	98·91	98·81	98·60

* A great number of these are of no use for cement making.

In certain works where the slags are rich in manganese it is possible to produce cements which may contain as much as 2 per cent. of this oxide, and these would tend to impart a brownish tint to the finished product.

Some Former Attempts to Employ Slags for Cement-making.—We cannot now afford sufficient space to do more than glance at a few of the various directions in which the problem of slag utilisation for cement production has been approached. Some have considered that by heating the requisite quantity of lime with the powdered slag a partial combination between the silica compounds and the added lime might be effected, and considerable success has been obtained by roasting processes on these lines in the United States. Others have endeavoured to bring about this combination in the wet way by grinding slag and lime together in a mortar-mill. It was thus that slag was employed for some time at Skinninggrove Iron Works in the production of cement concrete for the construction of a sea-wall, &c. Lastly, slag has been used on a very extensive scale abroad, intimately mixed with slaked lime, without recourse either to heat or moisture.

Slag Cement Prepared from Slag Sand and Lime.—As far back as 1862, Messrs. Lürmann & Langen, at Troisdorf, noticed that granulated slag was possessed of marked hydraulic properties, and in a report on tests of this material, dated March 12th, 1862, it is stated:—"From these experiments it follows that the cement prepared from granulated blast-furnace slag, with a moderate addition of lime, provides a most valuable material for use either in air or water, and furnishes a cementing agent which takes an intermediate position between Rhenish trass and Portland cement, being in fact much superior to trass." Lürmann made practical use of this discovery, and in 1865 he was engaged in the manufacture of paving blocks and artificial stone. These blocks were made of concrete, consolidated in hand or steam presses, and allowed to set for six or eight weeks, and this industry attained to considerable importance. It was not, however, until about 1880 that so-called "slag cement" or "puzzuolana cement" came into the market. Prof. Tetmajer, of Zurich, devoted much attention to the chemistry of these materials and to the treatment and manipulation of slag cements.

Slag Cement as a Kiln Product.—Considerable progress has been made both on the Continent and also in America in the production of cements from intimate admixtures of slag and lime, which, after having been calcined and clinkered in the kiln, are reduced to powder. This process is, as will be evident, in all respects analogous to the manufacture of Portland cement in the ordinary way, and renders the resulting material no longer liable to be classed as a puzzuolana cement, as is the case with those which are simple admixtures of slag and quicklime. We

believe that there are above ten or a dozen factories in Germany in which cements are prepared from slag on the following lines:—Slag sand, produced in the usual way from the slag derived either from grey or white pig iron, is dried and ground in tube-mills to an impalpable powder. It is also freed from a certain amount of metallic iron by a powerful magnet. Limestone is likewise ground separately in a similar way, and the two powders are then carefully mixed in the proper proportions to yield a suitable cement compound. This is done in an automatic weigher and mixer. The mixture is subsequently moistened with water and pressed into blocks or bricks, which are dried and burnt in cement-kilns with interstratified fuel; in fact, all the final stages of the manufacture exactly resemble those employed for producing Portland cement in the ordinary way. Cements prepared in this manner from slag will stand all the tests to which Portland cement is commonly subjected, and when mixed with normal sand they yield surprisingly good results. On analysis the proportion of lime is relatively low, ranging from 54 to 60 per cent.

Two plants in the United States, the one in Pittsburg and the other in Chicago, likewise produce cement from slag by calcining in a similar way a mixture of compact limestone and granulated slag. It has been suggested that cements thus prepared should in all cases rank as true Portland cement, but that cements made from a mixture of slag sand and slaked lime, when these substances do not undergo any subsequent roasting process, should be classed as slag cements.

Production of Slag Cement.—It has been estimated that no less than forty factories were engaged a few years back in the production of slag cement, ten of these being situated in France and twelve in Germany, but several of these works have since been closed. A recent writer asserts that there are nine plants in the United States making slag cement. Of these, two, as above stated, employ a roasting process. The cement made without firing is very light both in colour and weight, while slag cements, which have undergone the roasting process, are rather darker in colour than ordinary Portland. Slag cements are better adapted for use in water, or even in sea-water, than for purposes where they will be exposed only to the air; and, according to Le Chatelier, the alumina present in cement of this type does not undergo decomposition caused by the action of the sulphate of magnesia contained in sea-water in consequence of the relative abundance of metallic oxides which they contain.

Passow's Slag Cement.—A patent was secured in 1901 by Dr. Passow for the manufacture of cement by blowing air into liquid slag issuing from the blast furnace, whereby it is granulated, and needs no further treatment except reduction to an impalpable powder. It is

claimed that by this process the silicate is partially decomposed, and that the following reactions take place :—

$\text{SiO}_2 \cdot 2\text{CaO}$ yields $\text{SiO}_2 \cdot \text{CaO} + \text{CaO}$ and a certain amount of $\text{SiO}_2 + 2\text{CaO}$. We have thus mixtures of the di-calcium silicate with the mono-silicate and free lime and silica, enough of the former being set free to render the addition of more lime unnecessary. Only very basic slag from grey foundry pig can be used for this process, but if it can be practically carried out, and if Portland cement can be produced in this very simple way, it bids fair to revolutionise the manufacture.

Process of Messrs. Bosse & Wolters.—A successful process of making a cement resembling Portland cement from slag is that patented by Messrs. Bosse & Wolters, whose representative in this country is Mr. E. Larsen. Their invention consists in the selection of suitable slags, which are mechanically reduced to an extremely fine powder, and amalgamated in a machine of simple construction with a proportion of slaked lime. In the ordinary process 25 parts of slaked lime are added to 75 parts of powdered slag. The secret of success lies in the extremely fine grinding and the perfect amalgamation of the slag and lime. In carrying out the manufacture, the slag, as it issues from the furnace, is run into water, giving rise to the formation of so-called "slag sand." This material was patented many years ago by Mr. Charles Wood, of Middlesbrough. It is found that when the molten slag falls into water it behaves much in the same way that glass does when used to produce Prince Rupert's drops, it flies into countless sharp fragments, resembling sand, the individual portions, as they fall, take the form of a porous pumice-like mass, which is very friable and capable of being easily crushed into powder. Slag sand produced in this way has, however, certain disadvantages for the after processes to which it is subjected; it is, moreover, extremely retentive of water, and difficult to dry.

Process of Mr. Snelus.—Mr. G. J. Snelus, F.R.S., has described a process of making cement from slag, in which the moisture is expelled from the granulated slag by calcining it in a furnace, and he states that in the course of this process a notable quantity of sulphur, which is always present in slags as calcium sulphide, is gradually oxidised to calcium sulphate, accompanied by the evolution of sulphuretted hydrogen. The calcium sulphate, if present in moderation, beyond as we have seen tending to render the cement slow in its set, has no injurious action. The process of Mr. Snelus, which he has perfected, in conjunction with Mr. J. Gibb, does not involve the use of additional lime beyond that originally present in the slag. The following results in pounds per square inch were obtained on testing three samples of this cement neat :—

	7 days old.	28 days old.	3 months old.
No. 1.	420	470	600
No. 2.	370	560	650
No. 3.	390	530	720

We are not in possession of full details respecting the process of manufacture, nor have we an analysis of this cement, but Mr. Snelus stated in 1890 at the Society of Arts, London, that 100 tons of slag were being used weekly for this purpose.

Mode in which the Slag Sand is Prepared.—There can be no doubt, however, that the act of forming the slag sand in the manner above described has a considerable influence on the behaviour of the material in the presence of lime, for it is found that when slag is allowed to cool slowly in the ordinary way, and is then reduced by mechanical means to a fine powder, it no longer possesses equivalent hydraulic properties in conjunction with the added lime. It is, therefore, probable that the rapid cooling or “chilling” has some physical effect upon the ultimate molecules of the slag, causing them to assume a state in which they can more readily undergo chemical action. At the time of entering the water, and in the fierce ebullition which then takes place, there is, moreover, undoubtedly a certain amount of chemical action, for with the steam an appreciable volume of sulphuretted hydrogen gas is given off, due probably to the decomposition of the calcium sulphide present in the slag.

Mode of Manufacturing Slag Cement.—In preparing the cement under Messrs. Bosse & Wolters’ specification, the slag sand is first thoroughly dried, and to 3 parts by weight of the dry slag sand 1 part of dry slaked lime is added in an apparatus termed the homogenizer or closed ball-mill. The open or continuous ball-mill has been described and illustrated on pp. 125 and 126. The closed mill consists of a hollow drum or cylinder, which may be of various sizes, the interior circumference is lined with fluted cast-iron plates, and in this drum are placed a number of chilled iron or steel balls, about 1 inch or 1½ inches in diameter. The mixture of slag and lime is passed into the drum through a hollow trunnion, by means of a worm feeding apparatus, and when a full charge has been added, the aperture is closed and the cylinder is caused to rotate slowly on its axis, with the result that the contents are, by the constant collisions of the revolving balls on the fluted lining, pounded and reduced to an extremely fine state of subdivision, and at the same time most perfectly mixed. When this operation has been continued for an hour, or for such time as may be found sufficient to thoroughly grind the mixture, a door in the outer lining is opened and

the contents in the course of a few revolutions are ejected through a shoot into a bag or barrel; the balls being retained by a coarse grating. The charge thus produced is now ready for the market, not requiring to be sifted or handled in any way.

Manufacture is Economical.—It will be seen from this description that the manufacture of slag cement is an extremely simple one, needing but little skilled labour and a relatively cheap plant. The area needed for the works is small, and a French writer, who has had considerable experience, states that the entire cost of works and plant for an annual output of 6,000 tons (say 20 tons of cement per diem) is under £6,000, in which estimate he includes all the necessary buildings and an engine of 150 horse-power. This contrasts very favourably with the cost of works to produce an equivalent quantity of Portland cement by any of the existing methods, as will be evident from our estimates in Appendix E.

Features of Importance in the Manufacture.—There can be no doubt that this process owes its success—first, to the use of slag sand, which, as we have seen, possesses certain properties in which ordinary ground or pounded slag is deficient; and second, to the extremely fine grinding secured by the use of the homogenizer, which undoubtedly produces a truly impalpable powder. It must be remembered that in slaking the lime, if this operation is carefully conducted, with only just the proper amount of hot water, we obtain the hydrate, which constitutes 25 per cent. of the bulk of the cement, in a state of subdivision infinitely more minute than would be possible by any mechanical means, and the pumice-like friable slag sand lends itself admirably to the grinding process, and has its pores mechanically filled with the lime particles in the homogenizer. Experiments tend to show that whereas ordinary slag is unacted upon by water, it is possible by grinding it to a very fine powder in an agate mortar to obtain a substance which has feeble cementitious qualities; this is probably due to the liberation of particles of lime and other sparingly soluble bases which have become surrounded in the fused mass with a thin film of silicates.

Necessity for Extremely fine Grinding.—The urgent need of extremely fine grinding is shown by some tests at Choindez, which gave the following results:—

Measles per square inch.	Percentage Residues.			Age in Days.	1 Cement to 3 Sand.		
	A.	B.	C.		A.	B.	C.
5,806	7.1	0.5	0.0	...	...	...	...
16,128	16.1	2.0	0.5	7	131	227	341
32,257	28.9	18.0	8.4	28	230	419	537

In this table A, B, and C represent the same sample of cement ground in three different ways, and tested by sieves of three different degrees of fineness. Sample A was the most coarsely ground, in that on a very fine silk it left a residue of 28.9 per cent. On a corresponding sieve, the more carefully ground sample C left a residue of only 8.4 per cent. The sample A was ground as fine as it was possible by means of the mill-stones in common use in cement works. Sample B was passed through the homogenizer, and sample C was treated a second time in the homogenizer, so as to be reduced to the finest possible powder. The cement C, when tested with three parts of sand, proved to be more than double the strength of sample A, tested in a similar way. Portland cement can, of course, be dealt with by the homogenizer and gains greatly in tensile strength by the operation, but the improvement is chiefly noticeable when the cement is tested with sand. It will at once be seen that the finer the grinding the greater is the power of uniting together the sand particles, as the action of a cement depends to a very great extent upon the amount of surface that it will cover.

Properties of Slag Cement.—We may now glance at the properties of the slag cement, which differs to a marked degree from Portland, for while the specific gravity of a good sample of the latter would average about 3.10, that of slag cement never exceeds 2.75, the slag from which it is made having a specific gravity of about 3.00, and that of slaked lime being only 2.08, the diminished density being no doubt partly due to the porosity of the slag sand. A cubic foot of the slag cement weighs, therefore, about 75 lbs., or the bushel would weigh 90 lbs., being thus about 20 per cent. lighter than Portland cement. Slag cements are essentially of the slow setting type, rarely taking less than five hours for this purpose. They distinguish themselves from Portland chiefly from the fact that they reach their greatest degree of induration in less than twelve months; in fact, in many cases they show but little improvement after the first month. They test extremely well with sand, owing to the extremely fine grinding, and there is less difference between the tests of the neat cement and that with 3 parts of sand than is observed in the case of most samples of Portland cement. Owing to the slowness of the set they are ill-adapted for plastering and stucco, and they do not produce so hard a surface as that obtained by the use of Portland.

These cements behaved admirably under all the volumetric tests, and they will stand perfectly unchanged the various steaming and boiling processes for accelerated set. The German manufacturers have adopted for them the generic name of "Iron Portland Cement."

Slag Cement can be Stored with Impunity.—Slag cement compares favourably with other similar materials when stored for long periods. If freely exposed to the air, the available lime gradually unites

with carbonic acid, and this action is relatively much more rapid than is the case with Portland; thus, in four days a thin layer of slag cement gained about 5 per cent. of carbonic acid, the amount of this acid taken up in the same time by a similar sample of Portland cement was only 1 per cent. The slag cement does not, however, greatly deteriorate in tensile strength by prolonged storage, as the following experiment tends to prove:—A sample of the cement was tested with sand, and gave, at seven days, 254 lbs., and at twenty-eight days 340 lbs. per square inch, with 3 parts of normal sand. After being kept for fifteen months, and similarly tested, the figures were 243 lbs. at seven days, and 321 lbs. at twenty-eight days, showing, therefore, a loss in strength of less than 5 per cent. Slag cement yields such a fat rich mortar that it lends itself peculiarly well for works under water. Used for sea-walls, as has been done at Skinningrove, near Saltburn-on-the-Sea, it rapidly attains great hardness, and makes excellent work.

The Chemistry of Slag Cement.—The chemistry of the cement action in the case of this material is somewhat obscure, and tends to subvert certain of the theories which have been put forward to explain the induration of Portland cement. Before considering the question further we may glance at the following analyses:—

	Portland Cement.	Slag Cement.
Lime (CaO),	61·07	39·68
Silica,	21·70	24·34
Alumina,	8·60	18·74
Protoxide of iron,	...	0·27
„ manganese,	...	0·23
Peroxide of iron,	2·25	0·14
Magnesia,	1·17	6·59
Potash,	0·75	0·28
Soda,	0·42	0·44
Sulphur,	...	0·93
Sulphuric acid,	1·93	0·25
Carbonic acid,	0·80	4·07*
Water and loss,	1·26	4·70
Total,	99·95	100·66

Here we have in the first column a sample of Portland cement of average composition, and in the second an analysis of slag cement. If the carbonate of lime in the latter analysis is separately set down as lime and carbonic acid we have in the slag cement $39·68 + 2·28 = 41·96$ per cent. of lime, as compared with 61·07 per cent. in the Portland cement, though probably the 6·59 per cent. of magnesia in the former may be regarded as ranking with the lime.

* Carbonate of lime equal to lime 2·28, carbonic acid 1·79.

Proportion of Lime and Magnesia to Acids.—If we take the total percentage of lime and magnesia in both cements, equal to 48.55 in the slag cement and 62.24 in the Portland, we find that the equation of total lime divided by silica + alumina is roughly $\frac{3}{2}$ in the slag cement, as compared with $\frac{2}{1}$ in the Portland. This latter equation is fairly representative of the average composition of all good specimens of Portland cement, and we should at first sight consider it quite impossible that a cement having the formula of $\frac{3}{2}$ would give good results.

Composition of Slag Cement throws some doubt on Chemistry of Portland.—We are in fact compelled to reconsider certain of our theories respecting the action of the silicates and the relative proportion of lime required to obtain cementitious properties. It is probable that in the case of slag cement, at the very high temperature attained in the blast furnace (that of complete fusion), compound silicates of lime and alumina, together with small quantities of metallic and alkaline silicates, are produced, which, when taken alone, are almost entirely inert. That is to say, that when they are reduced mechanically to a fine state of subdivision there is but little tendency among the particles to form fresh compounds in the presence of water. The energetic action of hydraulic cements of the Portland type is largely due, as we have elsewhere shown, to the formation of hydrated aluminates and silicates of lime, which rapidly solidify the water used in making the mortar, and are said to set. In nearly all specimens of Portland there is undoubtedly a considerable margin of lime which readily gives up the alumina or the silica with which it is combined on the addition of water. It has frequently been described as "free lime," or even as "uncombined lime," though from recent experiments it is, as we have seen, very doubtful whether any good sample of Portland cement, or even of slag cement, contains much lime which can be spoken of as free lime. Some of this lime may, however, either have been present in the original mixture in excess of the requirements of the alumina or the silicic acid, or it may have become mechanically entangled in or coated with the vitreous, or semi-vitreous, silicates formed in the kiln.

Free Lime in Portland Cement.—It is difficult to estimate the exact proportion of this available lime, but we are warranted by what takes place in the case of slag cements to consider that the amount is considerably larger than chemists have hitherto thought possible. When Portland has been steamed or thoroughly "purged," and the whole of the available lime has been set free and hydrated, the cement loses its energy of set, and is rendered much safer and more reliable in its action. If, as Le Chatelier supposes, the chief active constituent of Portland cement is the tri-calcium silicate, and if on treatment with

water this silicate is, as he asserts, decomposed into two molecules of crystalline hydrate and one molecule of hydrated mono-silicate of lime; or if, as Meyer claims, on purely theoretical grounds, it splits up into two molecules of calcium hydrate and one of anhydrous mono-silicate, under either assumption there is a considerable margin of lime becoming capable of hydration. What takes place, when water is added to the mixture of pulverised slag and hydrate of lime in the slag cement, must be a partial decomposition of the sparingly soluble silicates of the slag and a mutual reaction between them and the lime, which latter in itself (being previously fully hydrated) is incapable of being further acted upon by water. The slag contains but little free lime, as it is but slightly attacked by acids, but there is no doubt a slow and gradual decomposition of the silicates and aluminates and the other bases present in the slag, and a reaction ensues between these silicates and the calcium hydrate, leading to the formation of fresh compounds of lime, silica, and alumina, which are not only themselves capable of induration, but possess also the power of uniting very considerable quantities of aggregates in the form of mortar and concrete.

Excess of Lime in Portland Cement.—If this theory could be regarded as accurate, it will be seen that it follows as a necessary consequence, either that in Portland cement a superfluity of lime is present (to the extent of something approaching 20 per cent.), or that in the slag cement, possibly in consequence of the high temperature of calcination, different combinations of the lime and other substances are obtained, which would, however, appear to be quite as stable and permanent as those prepared at a much lower temperature in the cement kiln. This fact has led both Dr. Michaelis and Prof. Zulkowski to suggest that it would be better to melt the cement clinker into slag in suitable furnaces rather than to stop short at the present stage of incipient fusion.

Theory of Cement Action needs Revision.—We cannot, however, escape the conviction that the behaviour of the mechanical mixture of silicates and calcium hydrate forming the slag cement throws considerable doubt upon those theories of cement action which imply that in Portland cement the induration is brought about by the hydration of ready formed aluminates and silicates, or that certain silicates of lime, alumina, iron, and the alkalis, produced in the kiln by the action of heat, are in the presence of water recombined or transformed into hydrated double silicates, since it is evident that in the slag cement, when produced by cold mixing, notable quantities of hitherto uncombined lime are united to the silicates of alumina or other bases present in the slag. The exact nature of the chemical changes which take place has, we regret to say, not yet been satisfactorily explained, though

numerous attempts have, as we have seen, been made to account for these reactions.

Other Considerations involved besides Chemical ones.—That other considerations besides purely chemical ones influence the behaviour of the slag is, however, shown by the following samples of slag sand, which when analysed gave almost identical results, but which, when treated in the same way and mixed with precisely the same amount of lime, gave widely different results. The composition of the slags was as follows :—

Ingredients.	A.	B.
Silica,	24·10	23·22
Alumina,	16·30	15·61
Lime,	46·53	47·10
Oxide of iron,	0·93	0·78
Soda, potash, &c.,	5·04	5·56
Carbonic acid,	0·65	0·85
Moisture,	6·45	6·88
Totals,	100·00	100·00

Tested with sand in the same way, the tensile strength of the cements produced by the addition of lime was—

1 Cement to 3 Sand.			
A.		B.	
7 days.	28 days.	7 days.	28 days.
Lbs. 326	Lbs. 431	Lbs. 150	Lbs. 208

showing a difference of over 50 per cent.

German Tests of Slag Cement.—In order to show the behaviour of this cement when tested, the authors consider that the following details of the examination of a sample made and sealed up in the presence of one of them and forwarded to the Imperial German Testing Station at Berlin in December, 1886, may be of interest, and it will serve also to show the very careful and searching manner in which such trials are conducted, and speaks well for the qualities of this material. The investigation is extracted from the *Proceedings of the Institution of Civil Engineers* :—

INVESTIGATION OF SAMPLE OF SLAG CEMENT CARRIED OUT BY THE ROYAL
TESTING-ESTABLISHMENT FOR BUILDING MATERIALS AT BERLIN.

Results of the examination of a parcel of cement forwarded on the 3rd December, 1886, marked "Sample of Cement," without further particulars as to locality. The tests were commenced on the 9th December, 1886, under the rotation number Spec. XVI., No. 4,764.

As a mean of three observations in each case :—

	Kilogrammes.	Lbs. per Cubic Foot.
1 litre of the cement lightly filled = . . .	1·042	65
„ „ „ shaked down = . . .	1·611	100·5
„ „ normal sand = . . .	1·640	102·3

The normal sand was obtained by the selection of the finest possible quartz sand, which was washed and dried. From it were removed all the coarse particles rejected by a sieve of 60 meshes to the square centimetre, and only the particles subsequently retained on a sieve of 120 meshes per square centimetre were employed.

The production of a suitable mortar needed 40 per cent. of water, 500 grammes of the cement being used. A slightly stiffer mortar required 36 per cent. of water; the temperature of the cement and the water being the same, and equal to that of the atmosphere of the laboratory, the rise of temperature on mixture was 0·7° Centigrade. It was made up into pats on glass, and set in 2½ hours, the average temperature throughout the experiment being 22·5° Centigrade.

Tested with the sieve, the following results were obtained :—

5,000 meshes per square centimetre, 14·0 per cent. residue.	
900 „ „ „	5·0 „ „
600 „ „ „	1·0 „ „
324 „ „ „	0·5 „ „
180 „ „ „	0·0 „ „

The tests for expansion and contraction were carried out by means of ten pats of neat cement, made up on glass and roofing-tile, and trowelled to a thin edge. The pats remained twenty-four hours in air, and were then placed in water. They kept perfectly true and sharp-edged, and were free from cracks. There was no expansion or contraction, and the cement adhered to the glass. When broken it presented a close even-grained and uniform fracture.

The briquettes employed to ascertain the tensile and compressive strength were made up on December 10, 1886, as follows :—

(a) The neat cement was mixed with 16½ per cent. of water.

(b) The sand briquettes were made of 1 part by weight of cement,

3 parts by weight of normal sand, and $7\frac{1}{2}$ per cent. of water. The mixture was beaten into metal moulds placed on glass plates in the usual way.

The temperature of the air was 22·5° Centigrade.

” ” ” water was 16·2° Centigrade.

The moisture of the air was 68 per cent.

The tests set the first day in air, covered up with writing paper to avoid too rapid desiccation; the remainder of the time they were in water. Taken from the water and tested they gave the following results:—

Mix- ture.	TENSION.						COMPRESSION.				Proportion of Tensile to Compressive Strength.	
	Close- ness after Filling.	Tensile Strength after				Close- ness after Filling.	Compressive Strength after					
		7 days.		28 days.			7 days.		28 days.			
		Ger- man.	Eng- lish.	Ger- man.	Eng- lish.		Ger- man.	Eng- lish.	Ger- man.	Eng- lish.	7 days.	28 days.
Neat.		Kils. per sq. cm.	Lbs. per sq. in.	Kils. per sq. cm.	Lbs. per sq. in.		Kils. per sq. cm.	Lbs. per sq. in.	Kils. per sq. cm.	Lbs. per sq. in.		
1 to 0	2·113	45·50	646·0	48·65	692·0	...	...	...	...	...	...	...
Sand.												
1 to 3	2·261	30·03	428·0	35·78	510·0	2·262	237·3	3,376	300·1	4,269	1 to 7·902	1 to 8·337

NEAT CEMENT (TENSION).

No.	7 days.		28 days.		Remarks.
	German.	English.	German.	English.	
	Kils. per sq. cm.	Lbs. per sq. inch.	Kils. per sq. cm.	Lbs. per sq. inch.	Made on metal plates, with 16½ per cent. of water.
1	44·25	629	48·25	686	
2	45·50	642	45·75	651	
3	43·25	615	53·00	754	
4	48·00	683	49·00	697	
5	44·00	625	48·00	683	
6	46·50	653	48·50	694	
7	45·75	651	48·25	686	
8	44·25	629	52·50	746	
9	48·00	683	46·25	657	
10	45·50	647	47·00	668	
Total, .	455·00	6,457	486·50	6,922	
Average,	45·50	646	48·65	692	

1 PART CEMENT AND 3 PARTS SAND (TENSION).

No.	7 days.		28 days.		Remarks.
	German.	English.	German.	English.	
	Kilos. per sq. cm.	Lbs. per sq. inch.	Kilos. per sq. cm.	Lbs. per sq. inch.	Made on non-absorbent plates, with 7½ per cent. of water.
1	31.50	448	38.25	544	
2	30.00	427	35.00	498	
3	28.50	405	36.50	518	
4	31.50	448	37.75	536	
5	29.00	412	35.50	505	
6	31.00	440	34.50	490	
7	30.50	433	35.75	508	
8	31.50	448	34.50	505	
9	27.25	387	33.50	476	
10	30.00	430	36.50	519	
Total, .	300.75	4,278	357.75	5,099	
Average,	30.07	428	35.78	510	

The briquettes were kept for the first day in the air, and the remaining time in water.

1 PART CEMENT AND 3 PARTS SAND (COMPRESSION).

No.	7 days.		28 days.		Remarks.
	German.	English.	German.	English.	
	Kilos. per sq. cm.	Lbs. per sq. inch.	Kilos. per sq. cm.	Lbs. per sq. inch.	Made on non-absorbent plates, mixed with 7½ per cent. of water.
1	229.6	...	287.8	...	
2	252.0	...	292.3	...	
3	237.4	...	305.8	...	
4	235.2	...	303.5	...	
5	233.0	...	292.3	...	
6	234.1	...	304.6	...	
7	229.6	...	291.2	...	
8	246.4	...	315.8	...	
9	230.7	...	292.3	...	
10	245.3	...	315.8	...	
Total, .	2373.3	...	3001.4	...	
Average,	237.3	3,376	300.1	4,269	

CHAPTER XVIII.

SCOTT'S CEMENT, SELENITIC CEMENT, CEMENTS PRODUCED FROM SEWAGE SLUDGE AND THE REFUSE FROM ALKALI WORKS, AND SIDERO CEMENT.

CONTENTS.—Discovery of Scott's Cement—Faraday's Opinion on the Theory of this Cement—First Patent for Scott's Cement—Influence of Sulphur on Lime—Selenitic Cement—Theory of this Cement Action—Tests of Selenitic Cement—Graham Smith on Sulphates—Cement from Sewage Sludge—Cement from Alkali Waste—Composition of the Cement—Cement from Caustic Soda Waste—Sidero Cement.

Discovery of Scott's Cement.—In the course of some attempts to produce an artificial hydraulic lime by calcining lumps of chalk in a common fireplace, about the year 1854, General (at that time Captain) Scott, R.E., found to his surprise that the calcined lime would not go abroad or crumble to dust in the usual way in water. Tested with acid, the lime was found to be properly burned, but it had lost its avidity for water. Captain Scott was thoroughly puzzled by this result, and he consulted Dr. Faraday in his difficulty.

Faraday's Opinion on the Theory of this Cement.—After careful consideration of the facts, that eminent chemist came to the conclusion that this change in the behaviour of the lime was due to the formation of some form of sub-carbonate of lime—a compound the existence of which previous investigators had suspected, and which was believed to confer new properties upon the calcined lime, the most important of these being the above mentioned failure to fall into powder when quenched or sprinkled with water.

First Patent for Scott's Cement.—So convinced was General Scott of the accuracy of this surmise that he was induced to patent the process provisionally in March, 1854, No. 735. In his specification he proposed to prepare a cement either by calcination, so applied as to drive off only a portion of the carbonic acid contained in chalk or limestone, leaving the substance in the state of sub-carbonate, or by subjecting ordinary quicklime or supercalcined lime to heat in the presence of carbonic acid, so as to bring it back to the state of a sub-carbonate. He also specified a third process of mixing quicklime and carbonate of lime in such proportions as to cause them to form, when properly treated, a sub-carbonate.

Behaviour of Lime due to Sulphur in the Fuel.—Subsequent experiments proved this invention to be founded on a misconception, and it was ultimately discovered that the change in the behaviour of the lime was due to the presence of small quantities of sulphate of lime, produced from the sulphur in the fuel. When the calcination was carefully carried out, and the resultant quicklime at a red heat remained for a short space of time in contact with brassy coal or impure coke, some of the sulphurous acid was absorbed by the glowing lime, and combined with it to form a sulphite, which ultimately passed into a sulphate of lime, and General Scott was the first to ascertain this peculiar action of sulphur compounds and sulphuric acid on quicklime.

Nature of Amended Patent.—General Scott at once perceived the importance of these new discoveries, and he took out a patent for converting lime of a partially hydraulic character into cement by the action of the fumes of burning sulphur. He effected this operation by reheating calcined lump lime in an oven, having a perforated floor, beneath which were placed pots of sulphur, the sulphurous acid from which ascended among the red-hot lime, leading to the formation of calcium sulphite, and this in turn became oxidised into the sulphate. The amount of sulphuric acid thus absorbed by the whole bulk of the lime was small, rarely exceeding from 2 to 3 per cent., and of course only the exterior surfaces of the lumps became coated with the sulphur compound, but when the lumps were ground, to prepare the cement for use, the sulphate of lime became evenly distributed throughout the mass.

Similar Results obtained in other Ways.—In course of time General Scott found that he could obtain the same results either by adding sulphuric acid to the water used in preparing the mortar, or by the addition of powdered gypsum or plaster of Paris to the ground lime. It little mattered in what form the sulphuric acid was conveyed to the lime, and many soluble sulphates were found to answer quite as well as the sulphate of lime.

Very small Amount of Sulphur required.—In laboratory experiments very minute quantities of sulphuric acid proved sufficient to control the avidity of caustic hydraulic lime for water. As little as $\frac{1}{4}$ per cent. of calcium sulphate only being needed if used in the water employed for tempering the mortar, while stirring in the lime, previously ground to a fine powder.

Selenitic Cement.—Ultimately General Scott specified the manufacture of a cement, which he named "selenitic cement," by the addition of 5 per cent. of ground plaster of Paris to calcined hydraulic lime, which was then ground to an impalpable powder and placed in sacks or

casks for use. The theory of the action of the sulphuric acid was originally supposed to be as follows:—That each molecule of lime combined with the sulphuric acid and water to form sulphate, and that the sulphuric acid then travelled on to the next molecule of caustic lime, which was in turn converted into a sulphate; the sulphuric acid traversing in this way the whole bulk of the lime, leaving behind it the calcic hydrate which has thus been formed without much evolution of heat and with no apparent change of volume. This action would be a species of cementation, but, in lieu of the above theory, a German chemist, Mr. F. Schott, propounds with a much greater show of reason, the following explanation:—

Schott's Theory of Selenitic Action.—The particles of gypsum in solution are mechanically deposited over the molecules of lime owing to surface-attraction. The coating of sulphate retards the access of water to the lime; it forms, if we may so style it, a temporary varnish, through which, however, owing to its solubility, the water speedily penetrates, and the molecules of lime then become hydrated, but this action is retarded to such an extent that the combination with water takes place gradually, without much evolution of heat, and with little or no perceptible increase of volume. The latter fact is proved by the much greater density of the selenitic hydrate than that of a hydrate formed in the ordinary way.

The paste formed by the selenitic process is sufficiently bulky to penetrate the interstices between the sand-grains and to bind together a large quantity of this sand into a mortar, though, of course, it is far less finely divided than the particles of fully slaked lime from which mortar is ordinarily made. The hydrate used for common mortar is, however, not really a binding agent in the true sense of the word at all.

Sulphur has no effect on Pure Limes.—If pure lime is treated in this way with a soluble sulphate no retarding influence is exerted, for the hydration takes place instantaneously before the coating is formed; it is only in the case of hydraulic limes, in which the combination with water is more gradual, that the coating of sulphate has time to form. Some interesting experiments by Mr. F. Schott, elucidating this theory, were published in Dinglers' *Polytechnische Journal*, in vol. clix, 1873, p. 30.

Feebly Hydraulic Limes best adapted for Treatment.—The selenitic process may be employed with advantage with all limes of a feebly hydraulic character, and it also greatly improves the eminently hydraulic limes of the lias formation. Limes of this kind, when made selenitic, will carry a largely increased volume of sand and give good results. Strong tough mortar and good plasterers' stuff may be produced from a mixture of 1 part of selenitic lime with from 4 to 6 parts of sand,

and it is a matter of common experience that any given sample of lime when prepared by the selenitic process will give double the tensile strength with twice as much sand, as when slaked and mixed into mortar in the ordinary way.

The Colour of Selenitic Cement.—In consequence of the fact that the lime does not become slaked when employed in accordance with General Scott's process, it retains its original colour, a warm buff, and the mortar is of course much more dense than one made from the hydrate. The power of binding together large volumes of sand is strikingly shown by the tests to which this material and the original Scott's cement have been at different times subjected.

Improvement Effected by Selenitic Process.—The improvement effected upon limes, when treated with a small percentage of plaster, as compared with the same materials when used in the ordinary way, is well seen in the following table, which gives some tests carried out at the New Law Courts, under the late Mr. Street, R.A. They were made by Mr. A. W. Colling, the Clerk of the Works. The resistances were arrived at by pulling asunder two bricks united crosswise, so as to give a joint having an area of $18\frac{1}{2}$ square inches. One month was allowed for setting. In every case the mortar was made in a mill, and the mean of three tests is indicated :—

Material and mode of preparation.	Proportion of sand to lime.	Mean resistance in lbs.
Lias gray lime as common mortar, . . .	3 to 1	112
„ „ selenitic „ . . .	6 „ 1	209 $\frac{1}{2}$
Barrow lime as common mortar, . . .	3 „ 1	125
„ „ selenitic „ . . .	5 „ 1	283 $\frac{1}{2}$
„ „ „ „ . . .	6 „ 1	196

Tests of Selenitic Cement.—From a large number of tests made by one of the authors to ascertain the strength of selenitic cement, as compared with Portland cement, the following have been selected because they clearly indicate the advantages of the selenitic treatment when carried out with suitable limes. The lias lime here used was that from Barrow-on-Soar, and the gray lime was from the Burham pits on the Medway. The whole of the samples were prepared by the late Mr. Hartley, who had a long experience in cement testing. The tests were in all cases made with ordinary stock bricks bedded across one another at right angles, giving a joint with an area of 20 square inches.

Nature of Material.	Age in Days when Frac-tured.	Parts of Sand to 1 of Cement or Lime.			
		3 Sand.	4 Sand.	5 Sand.	6 Sand.
Portland cement, .	28	...	463	325	313
Barrow selenitic, .	28	541	418	399	399
Burham selenitic, .	28	484	454	368	408
Portland cement, .	35	...	520	433	309
Barrow selenitic, .	35	435	539	438	430
Burham selenitic, .	35	424	430	490	556

Kirkaldy's Tests of Selenitic Cement.—By far the most important series of tests of this material with which we are acquainted was carried out for the Selenitic Cement Company by Mr. D. Kirkaldy in 1872. (See Appendix A.) He ascertained the resistance of selenitic cement exposed both to forces of tension and compression. In the former set of experiments he made use of test-briquettes having an area at the neck of 5 square inches, and also of bricks bedded crosswise, having a sectional area at the joint of 18·5 square inches. The blocks used for the tests in compression had a base area of 7·84 square inches. The test-briquettes of common lime mortar, when broken eight weeks after being made, showed a mean strength of 23·6 lbs. per square inch. Selenitic mortar, made from the same lime and with double the sand, attained in a similar time a strength of 83·0 lbs. per square inch. Blocks of common mortar crushed under a load of 121·7 lbs. per square inch, but when treated selenitically and used with twice the sand, the blocks withstood a load of 629·6 lbs. per square inch.

Experiment in Slaking Lime Powder.—The selenitic action is likened by Mr. Schott, to whose theories we have already alluded, to what takes place when dry, finely-powdered quicklime is tightly packed in a metal cylinder pierced with very minute perforations. If such a cylinder of lime is placed in water, which can then only reach the lime in very small quantities and very gradually, the lime is converted into a dense hydrate, which resembles in every way the hydrate formed by the selenitic process. This experiment would seem to confirm the accuracy of Mr. Schott's theory of the selenitic process.

Mr. Graham Smith's Observations on Sulphates.—It is much more difficult to understand the reason of the influence of sulphate of lime on slaked lime, as observed by Mr. Graham Smith, who, in a paper on "The Effect of Sulphates on Lime Mortar," has shown that calcium sulphate has a notable influence when mixed in certain

proportions with slaked hydraulic limes. In 1870, while he was in charge of the various cements and mortars employed in the works in progress at the Liverpool Docks, he carried out a large number of experiments with Halkin lime from Flintshire, a variety of white lias with fair hydraulic properties.

The analysis of this limestone is as follows:—

ANALYSIS OF HALKIN MOUNTAIN LIMESTONE.

Composition.		Percentage.
Substances soluble in acids— 74·726 per cent.	{ Carbonate of lime,	71·546
	{ Carbonate of magnesia,	1·348
	{ Protocarbonate of iron,	1·040
	{ Sulphide of iron,	0·792
	{ Alkalies,	
Substances insoluble in acids— 25·274 per cent.	{ Silicic acid,	20·068
	{ Alumina,	3·521
	{ Sesquioxide of iron, &c.,	1·192
	{ Water and carbonaceous matter,	0·493
Total,		100·000

The whole of the mortar used in the tests was mill-made, ground 30 minutes; the proportions indicated are in all cases by volume. The briquettes were of the ordinary shape, $1\frac{1}{2}'' \times 1\frac{1}{2}''$, or $2\frac{1}{4}$ square inches in area. They were broken in a Michele lever cement-testing machine. Corresponding tests were made with bricks bedded crosswise on the flat, giving a joint of $4\frac{1}{4}'' \times 4\frac{1}{4}'' = 18$ square inches, and the results though similar were scarcely so favourable to the sulphate mortar as the briquette tests which we have appended.

Common Slaked Lime Mortar Improved by Sulphates.—It will be seen that with $4\frac{1}{2}$ per cent. of sulphate, even with double the volume of sand, the mortar was much stronger than when lime alone was employed. It is to be regretted that no results are given with other proportions of sulphate. This mortar was found not to be adapted for use under water. The explanation of the foregoing results is surrounded with many difficulties, as the chemical action is quite different from that of selenitic cement, in which the slaking action is controlled by this means. We must probably seek for the solution in connection with the silica and alumina compounds of the Halkin lime, and it would be interesting to ascertain the behaviour of other hydraulic limes treated in a similar way.

EXPERIMENTS WITH HALKIN LIME MORTAR WITH AND WITHOUT SULPHATE OF LIME.

DESCRIPTION OF MORTAR.	Lime.	Sand.	Ashes.	Mixed with Salt or Fresh Water.	Number of Lbs. required to Break by Tension Briquettes of 2½ Square Inches.*			
					21 Days.	42 Days.	84 Days.	168 Days.
Ordinary mortar,	1	2	4	Fresh.	60	130	153	248
Do. do.,	1	2	4	Salt.	47	74	134	147
Do. with 4½ per cent. plaster,	1	2	4	Fresh.	98	141	340	375
Do. do.,	1	2	4	Salt.	67	183	232	387
Do. do.,	1	3	No ashes used with the Sulphate.	Fresh.	122	156	306	398
Do. do.,	1	3		Salt.	140	210	376	...
Do. do.,	1	4		Fresh.	97	154	299	422
Do. do.,	1	4		Salt.	100	190	401	...
Do. do.,	1	5		Fresh.	65	193	253	360
Do. do.,	1	5		Salt.	70	232	312	320

Cement from Sewage Sludge.—While treating of General Scott's cement, we must briefly allude to his proposals for the manufacture of cement from sewage sludge, a plan which was actually carried out upon a considerable scale at Birmingham, Burnley, Ealing, and several other towns, and one which enables the authorities to dispose of their sewage sludge with profit and advantage. This invention was a development of the so-called "lime process" of sewage treatment. In accordance with this process, a small quantity of slaked lime (from 15 to 23 grains per gallon) in a fine state of subdivision is added to the sewage water, and as this substance becomes mixed with the water in the sewer it gives rise to a copious precipitate, consisting mainly of carbonate of lime, together with a little phosphate of lime. The sewage is then allowed to pass into tanks where the flow is arrested, and the precipitate slowly sinks to the bottom, and in so doing it entangles and carries down with it nearly all the suspended impurities, leaving the supernatant water thoroughly clarified, and in a fit condition to be discharged into rivers of large volume. The sewage sludge or mud which remains at the bottom of the tank, when this clear effluent has been drawn off, is dried either on hot floors or by mechanical pressure, or other suitable means, and when sufficiently dried it is burnt in down-draught kilns of special construction, with small quantities of inter-stratified fuel.

Character of Sewage Cement.—General Scott was able to produce in this way a cement which had approximately the composition of Portland cement, because the detritus and clayey matters washed from the surface of the roads, and the ash of the faecal and other organic substances

* In all cases the average of three tests.

always present in sewage water, furnished the amount of silica, alumina, and iron needed for the cement. In dry weather it became necessary in certain cases to add a small quantity of clay to the sewage water along with the lime; this addition of clay aids in the clarification of the sewage, and need rarely exceed a few grains per gallon. This plan of dealing with sewage had manifest advantages, as it enabled municipal authorities to get rid of the sludge without expense, and lime is well-known to be the cheapest and best precipitating agent. It was found in practice that from 1 to $1\frac{1}{2}$ tons of quicklime were needed for the treatment of one million gallons of sewage water, or, say, for the daily volume of sewage produced by a population of 25,000 persons. If the cost of lime be taken at 15s. per ton, this implies a cost of 9d. per diem per thousand inhabitants. From each ton of lime used with sewage of average composition, there will result 30 tons of wet sludge or 3 tons of dry sludge. This sludge when calcined will yield about $1\frac{1}{2}$ tons of cement. It will be evident that, after undergoing calcination, all noxious matters will have been completely destroyed, and this plan of disposing of town sewage has thus many important recommendations from the hygienic point of view.

Difficulty of Drying Sewage Sludge.—One of the chief drawbacks encountered in carrying out this process upon a commercial scale was that the resultant sludge was extremely retentive of water and difficult to dry. The raw materials were also more fusible than the ordinary slurry, composed of lime and clay, in consequence, no doubt, of the large admixture of organic matter derived from the excreta; but we are of the opinion that this process, if it were efficiently carried out with the appliances now available for burning and grinding, would be found a successful and economical plan of disposing of the sludge, which has always been one of the main obstacles encountered in dealing with town sewage by treatment with lime.

Quality of Cement from Sewage Sludge.—The quality of the cement made in this way will manifestly greatly depend upon the composition of the sewage water, and on the impurities present therein. By carrying out the calcination at a lower temperature, the sludge may be converted into hydraulic lime, or a lime suitable for agricultural use. It was found by experiment that, for each ton of lime introduced into the sewers, 45 bushels of good agricultural lime, valued by Dr. Voelcker at 1s. per bushel, were obtained. The cement made at Burnley which was calcined at a high temperature, though it fluctuated somewhat widely in composition, owing to the varying quantities of detritus carried into the sewers during rainy weather, commanded a ready sale, and showed a fair degree of tensile strength. We believe that this valuable invention was somewhat in advance of its time, but that, with

the present state of our knowledge of cement manufacture, it could be carried out with complete success, and would prove a means of overcoming many of the difficulties in defecating town sewage.

Cement from Alkali Waste.—By means of certain patented processes Messrs. Chance are now enabled to extract from the alkali waste, resulting from the manufacture of soda on the Leblanc system, a very large part of the combined sulphur which was present as sulphate and polysulphides of calcium. This discovery may hereafter provide a mode of utilising those vast mounds of bye-products which now encumber the ground, and so sadly disfigure the vicinity of alkali works. In order to find some means of using the lime after the sulphur has been extracted, it has been more than once proposed to employ this material in the manufacture of Portland cement, but the percentage of sulphur still remaining in the waste has hitherto rendered this out of the question. By introducing a slight modification of the treatment one of the authors has succeeded in producing Portland cement from this material, and from a paper published by him in the *Journal of the Society of Chemical Industry* of June 30th, 1892, we have extracted the results of certain experiments made about that time with a sample of alkali waste which had the following composition :—

Coke,	2·492
Sand,	1·094
Silica,	1·156
Alumina,	0·926
Ferrous sulphate,	1·488
„ sulphide,	0·421
Calcium carbonate,	68·861
„ sulphate,	4·735
Magnesium carbonate,	2·428
Soda,	0·962
Water,	15·714

100·277

For reasons given below this material after being dried and ground was mixed with a marly clay, containing 30 to 40 per cent. of carbonate of lime, and a considerable excess of water, which was allowed to drain off; advantage being thus taken of the slight solubility of calcium sulphide. The dried slurry thus produced was found after careful calcination to yield a cement which stood high tests and gave good results when mixed with sand. As this substance proved very fusible, considerable care was needed in the burning, and the mixture with a clay rich in carbonate of lime was rendered necessary to bring down the proportion of calcium sulphate in the resultant cement.

Composition of the Cement.—The dried slurry was found to have the composition shown in Col. 1, and in Col. 2 we give the analysis of the cement :—

	No. 1.	No. 2.
Coke, water, and organic matter,	1·032	...
Sand,	1·349	2·749
Silica,	12·220	18·215
Ferrous oxide,	3·427	6·563
„ sulphide,	0·324	...
Alumina,	4·993	8·048
Calcium carbonate,	71·002	...
„ sulphate,	2·455	5·006
Lime,	...	56·682
Magnesium carbonate,	1·955	...
Magnesia,	...	1·639
Potash,	0·671	0·654
Soda, &c.,	0·772	0·779
	100·200	100·335

It was found in practice that if it is so far free from sulphur compounds as to give in the cement a quantity not exceeding 5 per cent. of calcium sulphate, alkali waste may, after treatment by the Chance process for the recovery of its sulphur, be successfully utilised for the manufacture of Portland cement. We learn, indeed, that Messrs. Chance have themselves established the manufacture of cement from their waste, upon a commercial scale, and that they are now producing considerable quantities of Portland cement of excellent quality from this material.

Production of Cement from Caustic Soda Waste in America.
—In order to work up the waste arising in soda manufacture, the Michigan Alkali Company, using the ammonia soda process and producing about 110 tons of waste per diem, erected a plant in 1899, from the designs of Messrs. Lathbury and Spackman, to convert the by-product into Portland cement. The residuum, which is pure white in colour and free from grit, is mixed with the bluish clay from the valley of the Detroit River. The following analysis shows the composition of the raw materials. Unlike the waste from Messrs. Chance's Works, the residuum from the ammonia soda process is practically free from calcic sulphate, but the percentage of magnesia was deemed to be excessive. The limestone at first used has, therefore, been discarded in favour of one with a much smaller quantity of magnesium carbonate, and the waste used as the lime ingredient now contains only about 1 per cent. of magnesia :—

WASTE.

Calcium carbonate,	74·85	} = 50·40 CaO.
Calcium hydrate,	11·24	
Magnesium carbonate,	8·24	} = 4·97 MgO.
Magnesium hydrate,	1·52	
Silica,	·98	
Oxides of iron and alumina,	1·62	
Sulphur,	·06	
Alkalies,	·50	
Total,	99·01	

CLAY.

Silica,	46·81
Oxides of iron and alumina,	14·21
Calcium carbonate,	25·07
Magnesium carbonate,	7·58
Sulphuric anhydride,	1·18
Alkalies,	3·04
Total,	97·89
Loss on ignition,	15·74

Very special attention has been paid in the design of the works to so arrange the plant as to be as nearly automatic as possible, and to avoid all resort to manual labour. The clay is first dried in rotary driers, and is then introduced in the requisite proportions into the liquid waste, and the mixture is pugged with additional water. The liquid slurry is then ground in tube-mills, so that 95 per cent. will pass a 200-mesh sieve. The slurry is pumped into rotary kilns, and burnt into clinker by coal dust mixed with air under pressure. The clinker at the discharge end of the kiln falls into a hopper-shaped concrete pit, whence it is raised by elevators into a specially-designed cooling bin. After final grinding in ball-mills and tube-mills, the cement is elevated and carried by an overhead conveyor into storage bins, from whence it passes to the packing machinery. The capacity of the plant is 450 barrels per diem.

Krupp's "Sidero Cement."—In consequence of the destructive action of sea-water, and of water containing sulphuric acid in solution, upon Portland cement, Messrs. Fried. Krupp have recently introduced a variety of cement, which they have termed "sidero cement," in which clays rich in alumina are replaced by iron ores or ores of manganese, and even chrome ore tailings and these are used in conjunction with chalk marl rich in silica. It was pointed out thirty years ago by Michaëlis and Schott that the alumina in cement mixtures might be

replaced by iron oxide, since the ferrite of lime and the manganite of lime harden just as well under water as the aluminate of lime, and Portland cement made under these conditions is no longer liable to the formation of the double salt, the silicate of lime and alumina, which crystallises with a relatively large percentage of water and with a considerable increase of volume, and which, owing to its high percentage of lime in combination with the alumina, is peculiarly exposed to the attacks of the magnesium sulphate present in sea-water.

By the selection of suitable ingredients rich in iron or manganese, which are incorporated with chalk marl containing very little magnesia and alumina, but with a high percentage of active silica, Portland cement may be produced by the dry process and calcined in rotary kilns. The mixture is so made that from two to three equivalents of lime are added to one equivalent of the hydraulic factors, $\text{SiO}_2 + \text{R}_2\text{O}_3$.

The mixture must be burnt to a clinkering heat, but as the calcium ferrites sinter at a lower temperature than the ordinary Portland materials, the cost of fuel is less than under the old process. The sidero cement clinker varies in colour from brown-black to black, and when ground it produces a light brown or a chocolate-brown powder, or, if rich in manganese, the powder will be black-brown in colour. The specific gravity is higher than is the case with the ordinary Portland cements, and may run from 3.25 to 3.35, and may even reach 3.44; this is due to the large percentage of iron present.

The chemical composition of the ore cement is indicated by the following analyses :—

	A.	B.	C.	D.
Silica,	21.785	23.841	19.901	22.243
Alumina,	4.431	2.852	3.548	1.602
Oxide of iron,	6.062	8.269	{ 9.643 }	11.138
Oxide of manganese,	1.814			
Lime,	64.476	62.830	65.557	62.416
Sulphate of lime,	0.888	1.239	0.602	0.995
Magnesia,	0.291	0.554	0.658	1.174
Potash and soda, } Not	...	...	...	...
Insoluble, } determined.	...	..	...	...
	99.747	99.585	100.059	99.568

Wherein one part by weight of the hydraulic factors (silica and oxide of iron and alumina) is respectively combined with 1.890, 1.906, 1.970, and 1.800 parts of lime.

The cement is relatively slow in setting, probably owing to the absence of the energetic action of the aluminate of lime, when treated

with water ; but after three days in water, the material attains a considerable degree of strength, and in the later stages of induration it even surpasses Portland cement in its resistance to crushing stress, which is in close accord with the density of the mortar.

Sidero cement perfectly withstands the action of sea-water, and it is also unacted upon by soda, lime, magnesia, and by iron sulphate. It can be mixed with considerable quantities of gypsum without any sign of expansion or disintegration, and it may be used with good effect with ordinary Portland cement, to which it imparts an additional degree of hydraulicity, and by this means the brown colour of the original cement may be varied to any shade from light grey to dark brown.

The following figures indicate the resistance of the new cement to tensile and crushing stresses in lbs. per square inch. A and B are samples of neat cement, and C is cement mortar, with three parts of normal sand. Each result is the average of ten separate tests :—

Age.	A.		B.		C.	
	Tension.	Com- pression.	Tension.	Com- pression.	Tension.	Com- pression.
3 days, .	414	5,600	415	...	143	1,657
7 ,, .	714	11,243	700	10,714	207	3,114
28 ,, .	794	14,885	857	15,500	371	3,428
90 ,, .	965	16,285	943	16,057	457	5,915
1 year, .	915	17,500	971	18,000	486	7,143
2 years, .	861	19,715	929	20,143	557	8,757

Tests which have been made with the sidero cement in sea-water show scarcely any traces of having been attacked, such as softening at the edges, blowing, or cracking, after exposure for two years, and it would appear that in this new material engineers have a reliable cement for marine constructions of all kinds.

CHAPTER XIX.

THE PLASTER CEMENTS.

CONTENTS.—Plaster of Paris as a Cement—Le Châtelier's Experiments—Preparation of Plaster—Plaster Kilns—Dumesnil's Improved Kiln—Coke-Ovens and Plaster Kilns—Use of Superheated Steam—Grinding of Plaster for Use—Gauging of Plaster—Researches by Landrin and Le Châtelier—Use of Alum—Keene's Cement—Martin's Cement—Staff.

Plaster of Paris as a Cement.—A whole series of cements, which have as their sole or chief ingredient sulphate of lime or plaster of Paris, depend for their set or induration upon entirely different properties to those which influence this reaction in the case of cements prepared from carbonate of lime. Calcium sulphate is found in a natural state in a great variety of forms, and is a substance of very common occurrence. As gypsum, the hydrated sulphate, the state in which it is perhaps most widely distributed, it contains in each 100 parts 32·60 of lime, 46·50 of sulphuric acid, and 20·90 parts of water, the chemical formula being $\text{CaOSO}_3 + 2\text{H}_2\text{O}$. There are numerous varieties of gypsum, some of them being transparent and crystalline as in selenite, some amorphous, and some fine grained and compact as in alabaster and plaster stone.

Calcic sulphate also occurs more rarely in the anhydrous state, devoid of water, when it is known as anhydrite, and it then consists of a crystalline mass with a regular cleavage into rectangular prisms. This mineral has not, so far as we know, been employed for industrial purposes.

Properties of Calcic Sulphate.—Sulphate of lime has a specific gravity of 2·31. It is slightly soluble in water (much more so than the carbonate). At a temperature of 60° F., 1 part of sulphate of lime will dissolve in about 490 parts of water. As the temperature rises the solubility increases until the water reaches 100·4° F., when the solubility again decreases. At the boiling point 1 part of sulphate will be contained in 571 parts of water, but by long-continued exposure to warm water the proportions may be varied somewhat considerably, and sulphate freshly precipitated is more soluble than gypsum. The raw gypsum or plaster stone is less soluble, moreover, than that which has been calcined. The industrial value of the sulphate of lime consists in the fact that the 2 equivalents of water with which we have seen that it is combined may be expelled at a temperature of about 392° F. A large part of this water may be driven off at a much lower temperature, and

where the material is reduced to powder and kept well stirred about three-fourths of the water may be expelled at a little below the boiling point of water, or about 205° F.

M. Le Châtelier's Experiments.—M. Le Châtelier, a French savant, who has recently carried out some interesting experiments in the dehydration of the plaster stone, and whose observations were communicated to the Académie des Sciences in 1883, has remarked that there are two distinct periods of rest during the process of expelling the water. His mode of demonstrating this fact was as follows:—Some pulverised gypsum was introduced into a hard glass tube, immersed in a paraffin bath, and gradually heated, the temperature being read off at regular intervals of time, by means of a thermometer imbedded in the plaster. By constructing a curve, showing graphically the increase of temperature for regular periods of time, it was seen that the heat rose rapidly to 230° F., then more steadily from 230° to 248°, remained for some time nearly stationary between 248° and 266°, then rapidly increased between 266° and 284°. A second, but minor, halt in the process took place between 320° and 338°. These two interruptions indicate the absorption of heat which accompanies the elimination of water, and point to the existence of two different hydrates, whose decomposition takes place at differing ranges of temperature.

The first of these compounds is represented by the formula commonly used for gypsum—viz., a hydrate in which 1 part of the calcic sulphate is combined with 2 parts of water $\text{CaSO}_4 + 2\text{H}_2\text{O}$. This substance parts with three-fourths of its water to form the second hydrate, in which 2 parts of the sulphate are united to 1 equivalent of water, which compound would be represented by the formula $2(\text{CaSO}_4) + \text{H}_2\text{O}$.

Commercial Plaster is a Hydrate.—The existence of this hydrate was clearly shown by M. Le Châtelier, for on heating for some time 10 grammes of powdered gypsum at a temperature of 311° F., which is intermediate between that needed for the decomposition of the two forms of hydrate, he ascertained that the loss of weight was uniformly 1.56 grammes, which corresponds very precisely with $1\frac{1}{2}$ equivalents of water, and from this it is clear that the compound thus obtained contains only half an equivalent of water, combined with the sulphate, or about 6.2 per cent. Ordinary commercial plaster of Paris as prepared for use contains, as a rule, about 7 per cent. of water, and hence it consists almost exclusively of this particular hydrate.

Plaster Burnt at High Temperatures.—On submitting the plaster to a temperature of 338° F. and upwards no change is apparent, so long as the heat does not exceed 390° to 430°, but beyond this point the material begins to lose certain of its essential properties. It ceases to absorb water with avidity, and sets only after a long interval of time. If the

heat reaches 650° it cannot be gauged in the ordinary way, and comports itself exactly like anhydrite. In this state it is termed "dead-burned."

Overburnt Plaster Combines very slowly with Water.—It has sometimes been asserted that plaster thus treated can no longer combine with water, but this is an error, as the hydration can still take place if the substance be reduced to a very fine powder; the process is, however, greatly retarded. On continuing the calcination of the plaster to the temperature of bright redness, the substance melts into a vitreous paste, which forms a crystalline mass on cooling, having all the attributes of anhydrite, which is no doubt a native gypsum, acted upon by volcanic or similar agencies. It is impossible to decompose this substance by heat, but if strongly heated in contact with charcoal, or in the presence of decomposed organic matters, it loses part of its oxygen and is converted into calcium sulphide, which substance is in turn acted upon by carbonic acid and water, giving rise to the evolution of sulphuretted hydrogen gas. It is in this way that we are able to explain the presence of sulphuretted hydrogen gas in certain mineral waters, originally containing sulphate of lime in solution. When waters rich in dissolved sulphate of lime are used in boilers, or when sea water is employed, a deposit or scale is formed, which consists mainly of the hydrated sulphate with half an equivalent of water, or one in which water is present to the extent of some 6 or 7 per cent. The mean of several analyses of boiler-scale from a marine boiler show this substance to have the following percentage composition :—

Carbonate of lime,	0.3
Peroxide of iron,	2.0
Water,	5.8
Sulphate of lime,	91.9
	100.0

Preparation of Plaster requires great nicety.—It will be evident from the foregoing observations that the preparation of plaster of Paris is a matter of considerable nicety, and that the degree of calcination requires attention and care, for while, on the one hand, too high a temperature produces a more or less inert substance; the failure to expel the water of hydration renders the material useless for moulding and casting, which, at any rate in this country, forms one of its chief uses. In many parts of France coarse plaster takes the place of lime mortar, and impure sulphates, or those mixed with small quantities of slaked lime, appear to be well adapted for this purpose. Moreover, precautions must be taken in burning the plaster to avoid direct contact with the fire, as carelessness in this respect leads, as we have seen, to the formation of calcium sulphide, a very objectionable product.

Preparation of Plaster formerly practised.—The oldest and simplest plan of burning plaster-stone, and the one which is still most commonly employed abroad is effected in a rude shed, enclosed on three sides by walls of brick or stone, and roofed in to protect the contents from the weather. As will be seen by Fig. 59, the floor is sometimes hollow, and

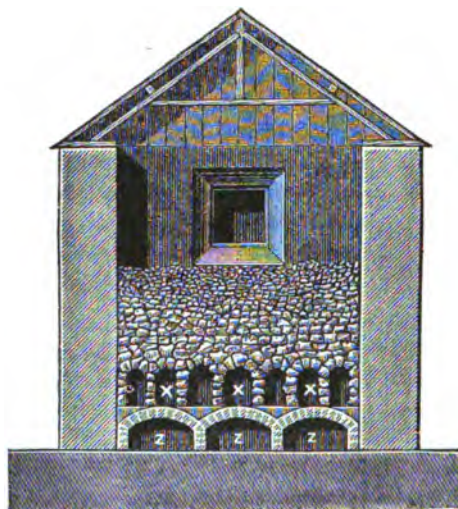


Fig. 59.—Covered Hovel for Burning Gypsum.

upon it the stone is built in a series of rough arches, x, x, x, disposed parallel to the main walls of the building; these arched flues are constructed of the largest lumps of stone, and immediately over them are placed the lumps next in size, the smaller pieces being next selected, and the size of the pieces of stone decreasing upwards as the heat from the fire diminishes, the top of all being covered in with dust and sweepings. Wood fires are then lighted in each flue, and these are regulated so as to produce a moderate heat, and they are kept going as steadily as possible in order to maintain an equable temperature throughout the entire mass of stone. The flames pass upwards through the interstices of the material and drive off the moisture and the water of hydration, which escape in the form of dense vapours, and pass out through openings in the roof and in the upper part of the shed.

Plaster Burnt with Coal.—When coal is employed in the calcination, rude furnaces are formed in the arched spaces beneath the floor, as seen at z, z, z in our illustration, and the flames pass through special apertures contrived in the tops of the arches. The firing is continued until the arch stones at the base of the mass show visible redness, say for about twelve hours, after which the fires are drawn and the plaster is allowed

to cool slowly. It will readily be seen that this plan is a very unscientific one, for while the top layers are often barely deprived of their combined water, the lumps forming the voussoirs of the arches are overburnt, and yield a partially if not wholly inert plaster. In spite of every care also, it is impossible to prevent the formation of a certain percentage of calcium sulphide, which gives rise to the unpleasant smell of sulphuretted hydrogen always apparent when plaster made in this way is gauged with water, and the presence of this sulphide is very unfavourable to the setting of the compound.

Preparation of Plaster in the Vicinity of Paris.—A much better system of dehydration is that practised in the vicinity of Paris, for which a kiln is employed somewhat resembling in form those used for

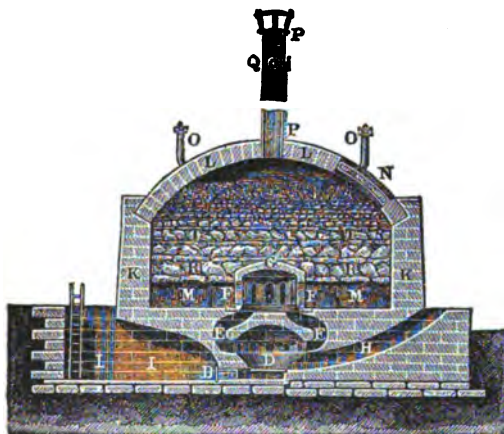


Fig. 60.—Transverse Section of the Dumesnil Kiln.

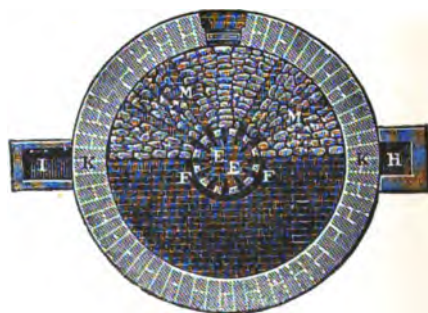


Fig. 61.—Plan of Plaster Kiln.

lime, but furnished with an arched cavity at the base, formed of fire-bricks and pierced with openings for the passage of the flame and heat. In a suitable kiln of this description the heat can be more evenly distributed, but it has the same objection as the one we have previously noticed, in that the bottom layers receive much more heat than those at the top, and the product, even with the utmost care, is never uniform throughout.

Plaster Kiln of Improved Construction.—A kiln which is much better in principle, in that the heat is under more complete control, and can be imparted more evenly to the whole of the contents, is that invented by M. Dumesnil, shown in Figs. 60 and 61. This kiln is circular in plan and has a central furnace, D, above which is the fire chamber, G, formed of fire-brick and furnished with twelve openings at F, F, F; the flame passes from the furnace into the chamber, G, by

curved flues, seen in section at E, E. Each of the openings at F is connected with a radiating flue, M, constructed with lumps of plaster built into the form of an arch. Above these flues the stone is arranged in layers, R, S, T, the larger pieces of stone being placed near the bottom and the smaller fragments in the upper layers. The top of the kiln is arched, and has one central and four smaller flues, all of which can be closed by means of dampers. In the arched roof, L, L, is an orifice, N, for filling the top of the kiln, while a door in one side serves for emptying and loading. The stoke-hole is shown at H, and the ashpit at I. In burning this kiln, which is 20 feet in diameter and 13 feet to the top of the arch, the contents are dehydrated by means of a moderate fire in about twelve hours, and then the fires are extinguished and an extra charge of 6 or 7 cubic yards of stone is added above the top layers, after which all the openings are closed, and the heat of the former charge is sufficient to effect the dehydration of the topping. The contents of this kiln are found to be about 45 cubic yards. The kiln is economical to work in the matter of fuel-consumption, and the products are fairly uniform in quality, but the first cost of its erection is very considerable.

Other methods of Burning Plaster Stone.—Various other plans for burning plaster stone have been from time to time introduced, some of them with a fair measure of success. Thus the waste gases from coke ovens have been utilised to heat the stone, and the arrangement of the kilns and ovens for this purpose is shown by Figs. 62 and 63. Here A, A, A are coke ovens of an ordinary type which discharge their surplus heat into a collecting flue, B. This flue communicates with a subsidiary flue, C, leading to the plaster kilns, D, D, D. It is possible, by means of dampers at E, E, E, to turn the heat into any one or more of a series of kilns. The floors of the kilns are perforated, and the flames pass up into the charge of plaster stone, which is piled up to a considerable height. The steam and waste heat finally escape by means of a collecting flue running along the tops of the kilns into the chimney, F.

Use of Superheated Steam.—Superheated steam and gas have also been employed successfully. When steam is used it is raised to a temperature of about 390° F. and blown alternately into each of two chambers filled with raw stone. The high temperature of the steam rapidly abstracts the water of hydration and leaves the plaster in a condition ready for grinding. Some experiments upon a small scale conducted by Mons. Violette led him to the conclusion that 3 cwts. of gypsum could be dehydrated in three hours by a current of superheated steam, amounting in weight to about 132 lbs.

Several processes have been brought forward for dealing with the

plaster stone in continuous kilns, or "running kilns," resembling somewhat those used by lime burners, and a process of roasting in cylinders caused to rotate, or furnished with a creeper or spiral screw, so as to move the plaster continuously forward from one end to the other, has also been tried. Many of these plans have resulted in the production of plaster of good and uniform quality, and free from the impurities and imperfections arising from the crude and unskilled processes in common use.

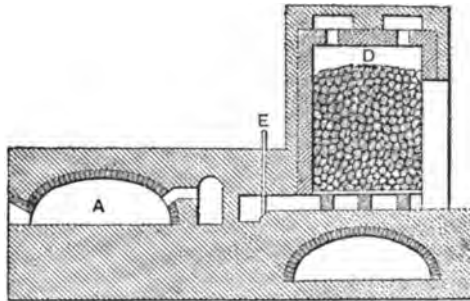


Fig. 62.—Section through Combined Coke Ovens and Kilns.

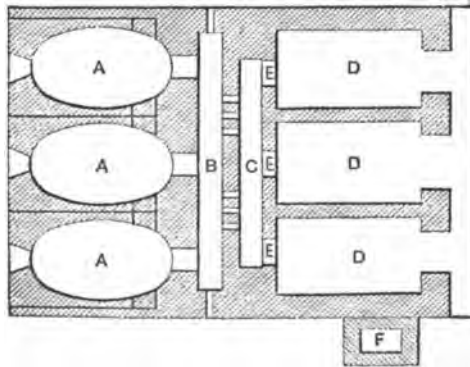


Fig. 63.—Plan showing Combined Coke Ovens and Plaster Kilns.

Best Plaster Prepared by First Grinding the Raw Stone.—For plaster of the best description, capable of setting quickly, and ensuring hard and durable casts, moulders prefer to obtain the raw stone for themselves, and to grind the same to a fine powder. This powder they then prepare for use by a so-called process of "boiling." The plaster meal is spread in a layer, some 2 or 3 inches in depth, upon a hot plate or in a shallow metal dish over a fire; in a short time, when the temperature approaches that of boiling water, a strange motion is communicated to the whole mass of the material, and the surface appears to rise up bodily as if suspended by the aqueous vapour given off by the lower layers. Little

openings or craters are formed all over the surface, and the steam passes off freely, mingled with fine dust. From time to time the plaster is stirred, and care is taken to avoid an excess of heat. When no further evolution of moisture takes place, which can be tested by holding over the surface a cold plate of glass or metal, to condense the steam, the heat is withdrawn, and the plaster is ready for use. When prepared in this way the combination with the water used for gauging takes place with great rapidity, and sound and hard casts are produced.

Plaster Baked in Special Ovens.—Much of the plaster used in this country is baked in ovens, constructed on the principle of the baker's oven. In this case the stone is broken into lumps about the size of a small hen's egg, and is introduced into a well-heated oven, the temperature being but little greater than that used in baking bread. It may be tested by inserting the hand, which should be able to bear the heat for two or three seconds. The oven is then closed up, and specimens are from time to time withdrawn, to ascertain if the dehydration is complete, the baking may last from twelve to twenty hours. The man in charge of the operation is able to judge, by the colour and appearance of the lump removed, if the water is expelled. Properly burnt stone exhibits on the white earthy fractured surface only a few bright specks here and there of crystalline particles, not completely deprived of the water of hydration. When the stone has been cooled it is ready for grinding.

The Grinding of Plaster for Use.—The grinding of plaster is a very simple matter, and almost any contrivance for this purpose will give good results. In some cases edge-runners or rollers are used, but the best meal is produced by mill-stones, such as are employed for grinding flour. Evenness and regularity of grain are most essential in the case of the best quality of plaster used for casting purposes. Such plaster has a soft, smooth feel to the touch, and sticks slightly to the fingers. It has, in fact, rather a tendency to cake together when compressed, while plaster which has not been sufficiently dehydrated has a dry and slightly gritty feeling. Overburnt plaster shows little tendency to absorb water, and cracks when made up with water. The ground plaster should be kept as far as possible from contact with the air, and not merely be placed in sacks, as is too often the case. The powder has a strong tendency to absorb moisture, after which it becomes slow-setting, and yields a less solid casting. In France heaps of plaster are sometimes kept in good condition for a long period (even for a year) by slightly wetting the outside of the mass with a watering can. By this means a preservative crust is formed which suffices to protect the interior of the heap.

The Gauging of Plaster.—The gauging of plaster, as the mixing of the same with water is termed, always gives rise to an elevation of

temperature, due to the hydration of the calcium sulphate, and this is a similar reaction to that which takes place when lime is slaked. We have seen that, in accordance with the temperature at which it has been burned, the gypsum is more or less fully deprived of its water of hydration, and that its recombination with water takes place with so much energy as to cause a considerable rise in the temperature of the mass. There is, at the same time, an increase in bulk, which may amount to as much as 1 per cent. in 24 hours after gauging. The volume of water employed has some influence upon the rapidity of the set, and upon the ultimate hardness of the plaster, but even with a very considerable excess of water the plaster has still the power of setting, which we know is not the case with quicklime. It is an axiom in plaster mixing that the plaster should be gradually introduced into the water used for gauging, and not the reverse as is sometimes the practice. While the mixture is being made the whole mass must be kept well stirred, by which means the formation of lumps and air-bubbles is avoided. The commonly received opinion respecting the setting of plaster is that the process is not only one of hydration, but that simultaneously a crystallisation of the mass takes place. The particles of the powder are converted into a porous network of crystals, which enclose in their interstices a certain proportion of the water containing sulphate of lime in solution. This water is held mechanically, and speedily evaporates, causing the dissolved sulphate to crystallise out, and thus adds to the hardness of the already-formed mass.

M. Landrin's Investigations into the Set of Plaster.—M. Landrin, who has investigated the behaviour of plaster with water microscopically, confirms this opinion, and assigns three distinct phases to the operation of setting. First, the plaster assumes on the contact with water a crystalline structure; second, the surrounding water dissolves a portion of the sulphate of lime; and third, a part of the liquid evaporates, owing to the rise in temperature caused by this chemical action, a crystal is formed and determines the crystallisation of the entire mass, in consequence of a phenomenon analogous to that which is observable when a crystal of sodium sulphate, containing 10 molecules of water, is thrown into a saturated solution of that salt.

M. Le Châtelier's Researches.—It appears that in 1883 M. Le Châtelier, in a communication upon this subject to the Académie des Sciences, pointed out that a direct transformation, according to the theory hitherto accepted, of the solid anhydrous sulphate of lime into the solid crystalline hydrated sulphate, would constitute an exception to the general law of crystallisation, and, moreover, the mere fact of crystallisation would not necessarily entail the aggregation of the mass. Thus, for instance, calcium sulphate, precipitated by means of alcohol from a con-

centrated solution, presents a maximum amount of entanglement of the crystals, but the precipitate when dried shows no tendency to cohere together into a solid mass.

New Theory as to the Process of Setting.—In order, therefore, to account for the setting of plaster and of other analogous substances, M. Le Châtelier has been compelled to formulate a new theory, based upon the phenomena of supersaturation investigated by Marignac.

Observations by M. Marignac.—This observer has shown that the hydrated calcium sulphate with half an equivalent of water, which remains undecomposed at a temperature of about 310° F., dissolves freely when shaken up with water, but that after a short interval the solution becomes turbid. This is due to the formation of a crystalline precipitate of the common hydrate with two equivalents of water, which has the formula of gypsum. The solution formed in the first case is five times as concentrated as that made from the less completely hydrated sulphate. It would appear from this that the most important agent in the accomplishment of the setting process is the relatively soluble hydrate—namely, that with a small percentage of water. This hydrate is at once dissolved, and then gives rise to the formation of the other hydrate, with the full equivalent of water. This latter compound decreases the solubility of the mixture, and the water becomes supersaturated with the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ hydrate, which crystallises out. This process continues so long as there remains any of the soluble hydrate $[2(\text{CaSO}_4) \cdot \text{H}_2\text{O}]$ to fortify the solution.

The set of plaster is thus the result of two distinct series of operations, which take place simultaneously; first the particles of calcium sulphate in the act of hydration are dissolved in the water used to gauge them and produce a supersaturated solution; the solution thus formed deposits crystals of the hydrated sulphate. These crystals gradually increase in size, and form a compact mass, in the same way as do all similar crystals deposited slowly from a saline solution, and this process is continued as long as any of the more anhydrous sulphate remains available to become dissolved and to keep the solution supersaturated.

Connection between this Process and the Induration of Cements.—This theory has, we believe, a somewhat important bearing on the set of calcium silicates, and the transference of the soluble lime to the crystalline silicates may take place in a somewhat similar way. It is on this account that we have reproduced, at some length, the valuable remarks of M. Duquesnay in the *Encyclopédie Chimique* treating of this subject.

Substances used to Improve Plaster.—It has long been known that a variety of substances are capable of imparting to the somewhat soft and friable composition of the set plaster a greatly increased hardness and consequent durability. Gay-Lussac has pointed out that the hardest

crude gypsum yields, after calcination and reduction to a powder, the hardest casts. This same property, so far as mortar was concerned, was, as we have seen, erroneously ascribed to dense and hard limestones. We learn from Tissot that if burnt gypsum, after it has become set, be repeatedly steeped in water and allowed to dry between each soaking, it will greatly improve the crystallisation of the mass and will result in a much harder casting. If six parts of plaster are intimately mixed with one part of freshly-slaked lime and used for casting purposes, and the object when made is steeped in a concentrated solution of magnesium sulphate, it becomes so hard, when dry, that it can scarcely be scratched with the finger nail. Various silicates in solution, as "water-glass," may also be used to harden plaster of Paris.

Alum used with Plaster.—The most common method, however, of hardening plaster depends upon the employment with it of alum, under a plan proposed, in the first instance, by Pauware, and improved upon subsequently by Greenwood. Alum may be used in two ways, either the finished casting may be steeped in a strong solution of alum, and then be slowly dried in a current of warm air—a process which needs at least a month in the bath—or the lumps of plaster when withdrawn from the kiln may be treated with a solution of alum, and then again raised to a red heat in a suitable kiln or oven. The heat in this second burning must be much greater than that needed for the dehydration of the gypsum. It is very necessary also that the heat during this second firing should be steady and uniform. The lumps when properly burnt have a dull milk-white or even a pale yellowish tint, but if the calcination is carried too far the lumps become as hard as stone, and are very difficult to reduce to powder. A composition of gypsum and alum, burnt at the requisite temperature, is readily ground, and when pulverised and gauged with water sets as rapidly as common plaster, but the resulting cement is not remarkably hard, unless the water employed consists of a solution of alum, containing from $\frac{1}{12}$ to $\frac{1}{15}$ by weight of alum. The casts obtained by this process continue to give off moisture or to "sweat" for a longer period than those made with ordinary plaster, but they acquire in time a degree of hardness comparable with that of alabaster or even marble, and they are capable of receiving a high polish. The surface has a creamy tint, and objects cast in this alum plaster, being much less soluble, will bear exposure to the weather, and will even resist the prolonged action of boiling water. It has been observed that these castings are to some extent semi-transparent, and transmit a certain amount of light through the thinner portions.

The Theory of the Action of Alum.—Various reasons have been alleged for this action of alum on plaster. Payen supposed that the induration was owing to the formation of a double sulphate of lime and

potash, the crystals of which were embedded in a precipitate of alumina, but this surmise has been controverted by the investigations of M. Landrin, who found by the analysis of numerous specimens of plaster treated with alum, both of French and English manufacture, that these substances were almost absolutely pure and free from alumina and potash. The results he obtained are seen in the accompanying table. Nos. 1 and 4 are French samples, and Nos. 2 and 3 are of English make.

Alum Cement.	Sulphate of Lime.	Carbonate of Lime.	Silica.	Water.	Total.
1, . .	96.75	1.05	0.72	1.48	100
2, . .	98.19	0.41	...	1.40	100
3, . .	98.02	0.37	0.42	1.19	100
4, . .	98.05	0.36	0.51	1.08	100

New Theory by M. Landrin.—Seeing that these samples were all so free from water, it may be assumed that they were in each case burned at a high temperature, and the absence of potash and alumina led M. Landrin to propound an entirely different hypothesis. He came to the conclusion that the action of the alum was caused by its contents in sulphuric acid, rather than by the bases present therein, and that this acid led to the conversion of the carbonate of lime into a sulphate of lime. In order to ascertain the accuracy of this surmise, he made use, in the first place, of a number of soluble sulphates, such as the sulphates of soda, potash, and ammonia, and caused them to act upon common plaster. He took care to employ only the precise amount of each of these substances which would furnish the supply of sulphuric acid needed to act upon the carbonate of lime, and he obtained precisely the same results as with alum. Parallel experiments, with sulphuric acid alone, gave, as he anticipated, corresponding results, and he was thus enabled to indicate a new process for the preparation of alum-plasters. All that is needed to impart the same degree of hardness as that due to the use of alum is to steep the raw plaster stone for about a quarter of an hour in a 10 per cent. solution of sulphuric acid and then to fire it at a dull red heat. By this means he obtained an excellent plaster cement, which left nothing to be desired in point of hardness, and which was sufficiently slow-setting. Moreover, the effect of the dilute acid was to destroy all traces of organic matter (always found in the raw gypsum, and which tend to give it a greyish colour), and to bleach it most perfectly, so that the resulting cement was exceptionally white and pure.

Importance of Expelling the Acid.—It must be remembered, in connection with this process, that it is absolutely essential that all the uncombined acid should be expelled, as even slight traces of sulphuric

acid would render the plaster more or less hygroscopic and liable to attract water. The burning should, on this account, be carried out at a temperature of from 1,080° to 1,260° Fahrenheit. As the effect of adding the alum is, as we have thus seen, merely to augment the amount of calcium sulphate present in the plaster, we can only attribute the slowness of the set to the influence of the high temperature at which it is burned, and there is thus a complete uniformity of action between the alum or sulphate plaster and that prepared in the ordinary way.

Keene's Cement.—Several other plaster cements have become widely known in this country, and they are for the most part prepared in a similar way to that we have described in the case of M. Landrin's process, only using a different solution. Keene's cement is made by steeping the calcined stone in a strong solution of borax and cream of tartar. The liquor is composed of 1 part of borax and 1 part of cream of tartar, dissolved in about 18 parts of water. In this solution the plaster in the lump, as withdrawn from the oven, is allowed to remain until it is thoroughly impregnated with the salts. It is then taken out, dried, and reburned at a temperature of dull redness for about six or eight hours. When cool it is ground to a fine powder, and it is ready for use. It is found that borax alone gives equally good results, and the more concentrated the solution into which the plaster is introduced the slower is the ultimate set. Thus, if to 1 part of a saturated solution of borax we add 12 parts of water, and employ this liquid as the bath, the set will take place in about fifteen minutes; but if only 8 parts of water be used, the cement will take at least an hour to set; and if 4 volumes of water be used, the cement will only become set after the expiration of several hours. The manufacture of Keating's cement is similar in all respects to the process employed by Keene.

Martin's Cement.—In the preparation of Martin's cement the solution employed is one of carbonate of potash, the stages of the manufacture being similar to those already described. For Parian cement, the bath employed may contain borax, but we understand that it is also prepared by calcining an intimate mixture of powdered gypsum and dry borax, which mixture is subsequently ground to a fine powder, which constitutes the finished cement.

Respecting the chemistry involved in the production of these cements, Knapp remarks that their action is probably due to the fact that one equivalent of water contained in the gypsum is capable of being replaced by a saline compound, and that possibly these substances have the power of completely taking the place of a portion of the water, and thus giving rise to the greater degree of hardness attained by the compound. A solution of tartrate of potash and soda (Seignette salt) causes plaster to set instantaneously. The indurated mass has the appearance of ordinary

gypsum, but it possesses the property, when it is repulverised, of again becoming hard when moistened with a solution of a salt of potash. Knapp's theory, it may be remarked, does not agree with that of M. Landrin. Many of these reactions are very interesting, and merit further study, which might lead to important industrial results.

Staff.—It seems necessary, seeing the vast extent to which this material is now employed for the purposes of decoration, and even for the construction of buildings of a temporary character, to say something of staff, which is a species of fibrous plaster, or plaster of Paris toughened and bound together with tow. In England this substance is generally known as fibrous plaster, as this was the name given to it by its inventor, Desachy, a French modeller, who took out a patent for it in 1856. It seems doubtful whether this was really a new invention at that time, but it has come to be very widely used for ornamental purposes, and at the Paris Exhibition of 1878 many of the most imposing structures relied upon this material for their decorative treatment, and the fibrous plaster was still more largely employed in 1900. The ordinary staff is made of plaster and Manila fibre, and the mixture is generally used upon a backing of coarse canvas, of very open texture, called "scrim." Any cheap fibre may be used, and for fireproof purposes the plaster may be incorporated with asbestos. For some purposes it is mixed with slag-wool or coke breeze. The moulds in most cases are made of gelatine on a plaster core. It is claimed that alum water applied to the mould at the time of casting hardens its surface, and causes the plaster to set more quickly; this would be in accordance with what has been previously stated with respect to alum solutions.

CHAPTER XX.

SPECIFICATIONS FOR PORTLAND CEMENT.

CONTENTS.—Differences prevalent in Specifications—Fine Grinding—Weight Test—Board of Works Specification—Mr. Grant's Proposed Specification—Mr. Michele's Specification—Specifications for Manchester, Salford, Blackpool, and Todmorden.

Differences Prevalent in Specifications.—There are few subjects concerning which English engineers are more at variance than cement specifications. In the course of a discussion upon this question at the Institution of Civil Engineers in 1880, Mr. William Gostling, the well-known manufacturer, gave the following examples of diversities of opinion of various engineers, as shown in the three cardinal tests of fineness, weight, and tensile strength. As will be seen, he analysed for this purpose 21 specifications:—

1. *Fineness.*

In 3 specifications, no mention of fineness.

5	„	finely ground.
1	„	very finely ground.
2	„	extremely finely ground.
2	„	residue not to exceed 10 per cent. with sieve of 1,600 meshes per square inch.
1	„	residue not to exceed 20 per cent. with sieve of 2,500 meshes per square inch.
1	„	residue not to exceed 15 per cent. with sieve of 2,500 meshes per square inch.
1	„	residue not to exceed 10 per cent. with sieve of 2,500 meshes per square inch.
1	„	90 per cent. to pass through a sieve having apertures of not more than $\frac{1}{16}$ inch in diameter.
1	„	no residue on passing through a sieve of 50 meshes to lineal inch.
1	„	80 per cent. to pass through sieve 5,800 meshes per square inch.
1	„	85 „ „ 5,800 „ „
1	„	fineness to be satisfactory to inspector; unsatisfactory if tests made from screened cement are stronger than those made from unscreened.

—
21 specifications, with 13 varieties of test.

Differences as respects Fine Grinding.—It was scarcely necessary, he said, to point out the inconvenience of requiring fine grinding merely in general terms. Such specifications betrayed an inadequate estimate of the value of fine grinding, and opened a wide field for disputes. Of the other specifications, two indicated the use of sieves of 40 wires per lineal inch, and three required sieves of 50 wires. In using these the percentages varied, and only one specification demanded complete sifting. An important specification, lately issued, assumed either that there was no appreciable difference between screened and unscreened cement, if finely ground, or that, if there was a difference, unscreened cement was the stronger, assumptions which were open to question. Then there was, as we see, an attempt to introduce the use of sieves of 5,800 meshes to the square inch, hitherto unused by the trade in England. All recent investigations in Germany and England demonstrate the importance of fine grinding, and surely it is time that this fact should be recognised, and that a uniform system, reconciling practice and theory, should be established and applied in drawing specifications.

2. *Weight per bushel.*

In 1 specification not less than 100 lbs. per struck imperial bushel.

1	"	"	110	"	"	"
8	"	"	112	"	"	"
1	"	"	114	"	"	"
4	"	"	115	"	"	"
1	"	"	116	"	"	"
1	"	about	118	"	"	"
1	"	not less than	108	"	nor more than 115 lbs. per imp. bushel.	
1	"	"	112	"	118	"
2	"	without any reference to weight.				

—
21 specifications, containing 10 varieties of tests.

Variations in the Weight Test.—Sixteen of these specifications placed no limit to excess of weight per bushel, merely guarding against undue lightness. One specification demanded a specified weight, and two specifications only adopted the more rational method of confining the weight within definite limits. There was no guiding principle apparent. The fact that the weight should bear a definite relation to the strength and fineness was not recognised, and weight of itself appeared to be deemed an indication of quality. The new specifications of one important public body discarded the test of weight entirely, rightly deciding that fineness of grinding and strength were the true tests. Assuredly if this test was to be retained, some kind of scale by which the relation between the weight and strength might be determined should be adopted.

3. *Tensile breaking strain, seven days after gauging.*

In 1 specification not less than 200 lbs. per sq. in., or 450 lbs. per 2½ ins. section

1	"	"	250	"	"	562½	"	"
2	"	"	267	"	"	600	"	"
5	"	"	300	"	"	675	"	"
1	"	"	311	"	"	700	"	"
1	"	"	333	"	"	750	"	"
2	"	"	350	"	"	787½	"	"
2	"	"	356	"	"	800	"	"
1	"	"	378	"	"	850	"	"
2	"	"	400	"	"	900	"	"
1	"	"	444	"	"	1,000	"	"
1	"	cement gauged with three times its weight of sand, to stand a strain of 140 lbs. per square inch twenty-eight days after making briquettes.						
1	"	cement gauged with 3 parts sand, to bear 150 lbs. per square inch twenty-eight days after gauging, if the cement sets neat in less than two hours, and 170 lbs. per square inch if taking more than two hours to set.						

—
21 specifications, embracing 13 varieties of tests.

Actual Points of Difference in the Twenty-one Specifications.—

Thus in these 21 specifications there were 37 variations in the tests, and as a great number of specifications would doubtless add to these variations, and admit of the three tests being combined differently, it becomes difficult to estimate the number of varieties in actual use.

Everyone who has had to do with Portland cement testing thinks himself able to devise a series of tests, and in the absence of any standard specification we obtain all these wearisome and vexatious differences of opinion.

Board of Works Specification.—One of the latest specifications of the former Metropolitan Board of Works read as follows:—

"The whole of the cement for these works, and herein referred to, is to be Portland cement of the best quality, ground so fine that the residue on a sieve of 5,800 meshes to the square inch (equal to about 76 per lineal inch) shall not exceed 15 per cent.* by weight. When tested, should the proportion which will not pass through the sieve be greater, a quantity of neat cement, equal to such excess, shall be added (at the contractor's expense), to the specified proportions of all cement, mortar, or concrete used upon the works. When brought upon the works it is immediately to be put into a dry shed or store, which the contractor shall provide for the purpose, having a wooden floor and all necessary subdivisions. The cement is to be emptied out upon the floor, every 10 tons being kept separate, and it is not to be used until it has been tested by samples taken from different sacks. The cement is to be gauged with three times its weight of dry sand, which has been passed through a sieve of 400 and been retained upon one of 900 meshes to the

* London County Council specification, 10 per cent.

square inch. The cement and sand having been well mixed dry, about 10 per cent. of their weight of water is to be added, and briquettes formed in moulds of 1 inch sectional area at the weakest point. The briquettes, having in the meantime been kept in a damp atmosphere, are to be put into water twenty-four hours after they have been made, and remain in water until their tensile strength is tested by means of apparatus belonging to the Board and by their officers. These briquettes must bear, without breaking, a weight of 230 lbs.* per square inch, twenty-eight days after the briquettes have been made; and the cement neat must not, at any season of the year, set in less than one hour. Any cement which does not answer the requirements will be rejected, and must be forthwith removed from the works. Briquettes of neat cement shall also be made and broken after seven days, as may be directed by the engineer. Their limit of resistance and the weight of the cement shall also give results to his approval. The cement store to be provided with a Chubb's patent lock and key, to be obtained and fixed by the Board."

The specification issued by the London County Council is, with a few trifling exceptions, to some of which we have drawn attention by footnotes, almost identical with the above. They state, however, that—

"Besides these mechanical tests, the cement will be tested as to its chemical character and as to the specific gravity, which is not to be less than 3.10."

There is also a note in the following terms:—

"To secure due progress the contractor shall, immediately after the contract is signed, procure and deliver on to the site of the works a stock of cement sufficient for carrying on the works for at least five weeks, and at all times, until their approaching completion, shall keep stored on the works a quantity equal to five weeks' consumption."

We, no doubt, owe all of these specifications to Mr. Grant, and it is, therefore, advisable, while we are on this branch of the subject, to reproduce the skeleton form of specification which he appended to his paper at the Institution of Civil Engineers in 1880.

Mr. Grant's Form of Specification for Portland Cement.

CEMENT-MORTAR AND CONCRETE.

"*Portland Cement.*—The whole of the cement for these works, and herein referred to, is to be Portland cement of the best quality,† ground so fine that the residue on a sieve of ‡ meshes to the square inch shall not be more than § per cent. by weight. Should the residue be greater, a quantity of cement proportionate to such excess must be added. When brought upon the works it is to

* L. C. C. specification, 250 lbs. per square inch is applied at the rate of 200 lbs. per minute.

† Here, if desired, the words may be inserted "weighing not less than 112 lbs. to the bushel."

‡ Either 6,400 meshes to the square inch = 80 to the lineal inch, or 5,806 per square inch = 76.2 to the lineal inch, which corresponds with 900 per square centimetre.

§ The residue may be either 20 per cent. as in the German rules, or 10 per cent. as in their practice.

be put into a dry shed or store which the contractor is to provide for the purpose, having a wooden floor and all necessary subdivisions. The cement is to be emptied out upon the floor, every [] bushels being kept separate, and it is not to be used until it has been tested by samples taken from different sacks.

"Testing.—The cement is to be gauged with three times its weight of dry sand, which has passed through a sieve of 400, and been retained upon one of 900 meshes to the square inch. The cement and sand having been well mixed dry, about 10 per cent. of their weight of water is to be added, and briquettes formed in moulds of 1 inch sectional area at the weakest part. The briquettes having in the meantime been kept in a damp atmosphere are to be put into water twenty-four hours after they have been made, and remain in water until their tensile strength is tested by means of apparatus belonging to the Board, and by their officers. All cement that, when neat, sets in less than two hours, must bear without breaking, when subjected to this test, a weight of * lbs., and if it take from two to five hours to set neat, it must bear a breaking weight of [170] lbs. per square inch twenty-eight days after the briquettes have been made. If not, it will be rejected, and must be forthwith removed from the works.†

"Cement-mortar.—The cement hereinbefore described, excepting as herein otherwise specified, shall for mortar be mixed in the proportion of 1 bushel or 112 lbs.‡ of cement to [two] bushels of sand.

"Cement Concrete.—The whole of the concrete to be used throughout the works is to be formed of Imperial bushels or cwts. of 112 lbs. of Portland cement to 1 cubic yard of ballast. The materials to be turned over three times in a dry state; the water then to be added, and the mass turned over three or four times more and thoroughly intermixed."

Specification proposed by Mr. V. de Michele.—Mr. V. de Michele, an engineer of great experience, and a manufacturer of cement, has proposed the following very concise tests, which he considers would be sufficient if embodied in a specification to "ensure Portland cement of the highest quality at market rates":—

Pats $\frac{1}{2}$ -inch thick in water, absolutely sound at 7 days.

Tensile strength, 400 lbs. per square inch at 7 days.

Fineness, 10 per cent. residue on a 50 sieve.

Note.—The pats to be gauged on glass, immersed in water immediately, and left there for the whole period. One pat to each three bricks.

The test bricks to be gauged by a skilled man, with any quantity of water, in any way he likes. The average of three to be taken, which shall represent about 100 tons or less. The strain to be applied as quickly as possible.

The sieve to have 2,500 holes per square inch, and to be of wire $\frac{1}{16}$ th of an inch in diameter. Shaking to be continued until nothing ground in the mill passes.

* Here insert either 142 lbs. = the German minimum of 10 kilogrammes per square centimetre, or a higher number, especially if the cement, neat, takes more than two hours to set.

† If a test for neat cement is inserted, the following words may be added here—"tested neat, the cement must bear a tensile strain of at least 400 lbs. per square inch, after seven days, six of them in water; and 550 or 600 lbs. per square inch after twenty-eight days, twenty-seven of them in water."

‡ The contractor may either measure or weigh the cement.

There is no doubt that from the manufacturer's point of view such tests would be deemed sufficient, but we consider the test of fineness altogether too lenient, while the immersion of the pat in water directly it is made is only practicable in the case of quick-setting cements.

Some English Specifications for Portland Cement.—As indicating the wide difference of opinion that still exists on this subject we append a few recent specifications for the supply of cement.

City of Manchester—Rivers Department.

Specific Gravity.—Not less than 3.05.

Fineness.—All shall pass through a sieve of 1,600 meshes per square inch, not leaving more than 5 per cent. residue on a sieve of 2,500 meshes per square inch, or more than 10 per cent. on a sieve of 5,625 meshes per square inch.

Tensile Tests.—Test blocks or briquettes shall be made with 20 per cent. of water, and the mixture shall be placed in a mould, without ramming, and kept for twenty-four hours in a moist atmosphere at not less than 40° F., and afterwards placed in water at a temperature of not less than 40° F.

These briquettes shall bear a stress before breaking of not less than 350 lbs. per square inch after seven days, and not less than 450 lbs. per square inch after fourteen days.

The moulds shall be filled with a steel-pointed trowel $3\frac{1}{4}$ inches long, and no other instrument shall be used for filling them. Any ramming of the cement into the moulds by hand or any other instrument shall not be permitted.

Set.—The cement shall, when mixed in pats with 20 per cent. of clean water, take not less than two hours nor more than eight hours to set hard.

Soundness.—Similar pats of neat cement, subjected immediately they are made to a moist heat of 90° to 100° F., and as soon as set placed in water at a temperature of 100° to 110° F. shall not show any signs of blowing after forty-eight hours' immersion.

Chemical Analysis.—A sample of the cement shall not contain more than $1\frac{1}{2}$ per cent. of magnesia, $1\frac{1}{2}$ per cent. of sulphuric acid, and 2 per cent. of insoluble residue. The loss on ignition shall not exceed 2 per cent.

The lime shall not be less than 58 per cent. nor more than 62 per cent., and the iron oxide and alumina together not more than 12 per cent.

Adhesion.—The cement, when made into a pat of 3 inches diameter and $\frac{1}{4}$ inch thick, shall, after the expiration of seven days, adhere firmly to the natural surface of a Welsh slate, the slate having been soaked in water prior to the application of the cement, and having been kept moist during the interval.

Expansion and Heating.—The cement shall not be considered ready for use if, when made into a paste and put into a test tube, it shrinks away from the sides in setting, or if the test tube be cracked in so doing, or if the rise in temperature be greater than 6° F. during one hour after mixing.

City of Manchester—Tramway Department.

Weight per Bushel.—Not less than 110 lbs. nor more than 117 lbs. to the Imperial striked bushel when filled by a Fajjas machine.

Fineness.—Not more than 5 per cent. residue on a sieve of 5,625 meshes per square inch.

Tensile Strength.—Briquettes made with at least 18 per cent. and not more than 27 per cent. by weight of fresh water shall bear a tensile strain of not less than 420 lbs. per square inch after being exposed to the air for six hours in a humid atmosphere at a temperature of 60° F., and subsequently immersed in water for six days. The moulds shall be filled with a steel-pointed trowel 3½ inches long, and no other instrument shall be used in filling them.

Soundness.—Pats of neat cement subjected immediately they are made to a moist heat of 90° to 100° F., and as soon as set placed in water of a temperature of 100° to 110° F., shall not show signs of blowing after forty-eight hours' immersion.

County Borough of Salford—Tramways Committee.

Fineness.—Samples of cement shall be sifted through a No. 180 mesh sieve—i.e., 32,400 holes per square inch—and shall not leave a residue of more than 9 per cent.

Tensile Strength.—Samples of pure cement will be gauged with water, and placed in the brass moulds used by the Corporation. Within twenty-four hours the casts thus made will be immersed in still water, in which they will remain for seven days from date of moulding, when they will be taken out of the water and tested to ascertain their tensile strength, which must not be less than 1,120 lbs. on a sectional area of 2¼ square inches—i.e., 1½ inches by 1½ inches square.

Time of Setting.—In order to ascertain the time of setting, a modification of Vicat's needle will be used, having an area of 1,400th part of a square inch, and a total weight of 2½ lbs.

Slow-setting cement must take an impression from this needle when standing vertically upon it at any time within three hours after moulding. Quick-setting cement must take the impression only during the first half-hour.

Corporation of Blackpool—Sea Wall and Promenade Extension.

Tensile Tests.—An average of not less than three test briquettes from every 10 tons of cement shall stand not less than 350 lbs. per square inch (Arnold's test) after being twenty-four hours in moist air and afterwards six days in water, and no briquette shall stand less than 300 lbs. per square inch.

Hot-water Test.—An average of not less than three test briquettes for every 10 tons of cement, made of one cement to three of sand, after being twenty-four hours in air and six days in water at 170° F., shall give no indications of unsoundness or cracking.

Fineness.—Ninety-five per cent. of the cement shall pass through a sieve containing 5,800 holes per square inch, and there shall be not less than 42 per cent. of impalpable flour as tested by the flourimeter.

Setting.—Pats made of neat cement to set in not less than twenty minutes or more than one hour.

Soundness.—Cement mixed with water to the consistency of treacle when put into a bottle shall not fracture the bottle and shall not become loose.

Adhesion.—A pat of cement 3 inches in diameter and ½ inch thick shall, after seven days, adhere firmly to the natural surface of a Welsh slate.

Todmorden Corporation Water Works.

Fineness.—The cement shall be proved to have been uniformly and sufficiently ground by sieving samples thereof through a sieve, the gauze of which shall weigh about 3·36 ozs. per square foot, and have meshes of 50 brass wires per lineal inch through which at least 95 per cent. of such cement shall pass freely.

Tensile Strength.—Strength briquettes of 1 square inch minimum section shall be made in suitable moulds without any abrupt angles, and should any mould become enlarged or otherwise distorted, such mould shall be forthwith rejected, and a proper mould substituted therefor. Six of such briquettes shall be moulded at the same time from a mixture made at discretion from each 10 tons or thereabouts, and after being moulded shall be kept in a damp atmosphere for about twenty-four hours, and shall then for about five days be kept in water. About seven days after moulding the ultimate tensile strength of each inch briquette shall be ascertained by loading continuously and at a uniform rate of about 3 lbs. per second, and at least one out of the six briquettes shall sustain without fracture a weight of 400 lbs. for not less than one minute.

Soundness or Condition.—10 ozs. of cement shall be rapidly mixed around the naked bulb of a sensitive thermometer with 3 ozs. of water in a white glazed jar (about 4 inches deep and $3\frac{1}{4}$ inches internal diameter, with the inside bottom approximately hemispherical), the cement, the water, the vessels and any other apparatus used having been previously brought to the same temperature as that of the air of the room in which the test is conducted, and the jar and its contents shall be protected from draughts during the test, and the rise of temperature of the cement within fifteen minutes of the mixing shall not exceed 2° F. nor within sixty minutes 4° F.

This, we believe, is Mr. G. F. Deacon's specification.

We hesitate, with all these differences of opinion, to give our own views as to a model specification. We can only hope that unanimity may ere long be established, and that the adoption of a uniform system of testing may lead to the use of a standard form of specification. Quite recently the Cement Section of the American Society for Testing Materials has issued a report on standard specifications for cement. This report we give in Appendix D.

and of similar specimens of PATENT SELENITIC MORTAR.—*See Woodcuts.*

PULLING STRESS.							
COMMON MORTAR. "Gauged."			SELENITIC MORTAR.				
Position.	Test No.	Stress, lbs.	"Gauged."			"Pressed."	
			Composition.	Test No.	Stress, lbs.	Test No.	Stress, lbs.
, Sand 3,	G		Lime 1, Sand 4,	G		G	
	671	169		684	392	682	477
	672	159		683	383	681	440
	673	123		685	305	680	381
, Sand 2,	670	129	Lime 1, Sand 4,	702	380	695	473
	667	116		701	358	698	418
	668	104		699	342	696	403
, Sand 4,	676	98	Lime 1, Sand 5,	692	289	687	438
	675	94		691	209	688	376
	677	71		694	202	689	326
	Mean	118		Mean	318	Mean	415
Per square inch	of area	23.6	Per square inch	of area	63.6	Per sq.in.	83.0

Dimensions 2.5 x 2.0 in.



Sectional Area 5.0 square ins.

specimens. They were all similarly tested eight weeks after preparation.

(Signed) DAVID KIRKALDY.

Appendix B.—The Effects of Sea Water on Cement.

We may summarise Mr. Carey's remarks on the action of sea water as follows:—He put the case thus, "The quantity of magnesium in sea water, present as chloride and sulphate, amounts to 0·06 per cent. by weight. In a porous mass of concrete, a precipitation of the salts of magnesia takes place, some of the lime of the cement being at the same time dissolved. On the one side, it is held that these salts of magnesia, filling the pores and interstices of the concrete, subsequently undergo a change of volume, producing disintegration. On the other hand, it is asserted that these precipitates are absolutely inert, and do not in any way affect the strength of the concrete." The views of Dr. Michaelis respecting the injuries likely to arise from the presence of magnesium salts (from quite another aspect), are quoted and it is admitted that he regards the rejection of cement containing over 5 per cent. of magnesia as advisable, owing to the acids with which this body is combined. Dr. Michaelis has, however, reported that Portland cements in which "magnesium was present to the extent of 20 per cent. were under his observation for ten years and showed no signs of flaw." Special tests made to determine the action of magnesia led Dr. Michaelis to regard this substance as a species of adulterant, when it took the place of a corresponding percentage of lime. He states that it is not actively useful in cements, but that it does not lead to changes of volume greater than those which occur in normal cement with up to 3 per cent. of this material, even when present to the extent of 18 or 20 per cent. Mr. Messent's views are quoted, and he asserts that the failures at Aberdeen were neither due to the use of cement of defective quality, nor to the practice of regauging and breaking up partially set concrete which had not been resorted to upon this part of the works. He attributes the injuries to the porous nature of the coating of the blocks, and he brings forward the theory of the deposition of magnesia from sea water, its consequent expansion and hence the disruption of the work.

Mr. Carey conducted a series of experiments to test the action of sea water on cement, and for this purpose he made 120 briquettes, some with neat cement and some with 1 part of cement to 2, 3, and 4 parts of sand. An equal number of tests was made of each series, and the whole of them were placed in a wooden cage and secured at the level of low water of ordinary spring tides at the pier-head at New-haven Harbour forty-eight hours after gauging. They were thus exposed not only to a constantly varying pressure due to the tidal movement, but also to the action of the waves at low water. They were all carefully weighed and submerged for periods which varied as follows:—Fourteen days, twenty-eight days, three months, and six months. They were then surface dried by exposure in the air and weighed afresh. The results are summarised in the following table and are somewhat contradictory, for, as will be seen, there is a slight gain of about 5 per cent. in fourteen days, while at twenty-eight days and at three months there would seem to be a reduction in weight which is made good, however, at the end of twelve months:—

TABLE SHOWING INCREASED WEIGHT OF CEMENT BRIQUETTES.

PROPORTIONS.	14 Days.	28 Days.	3 Months.	6 Months.
	Per cent.	Per cent.	Per cent.	Per cent.
Neat,	4·98	2·69	1·25	12·06
1 to 1,	4·53	2·23	0·38	9·57
1 to 2,	5·06	2·25	0·51	9·29
1 to 3,	6·16	2·25	2·51	10·2
1 to 4,	4·97	2·42	3·41	12·77

In spite of these fluctuations in the weight, the strength of the briquettes steadily increased with age, though most of the three months' tests show a small falling off; thus equal parts of cement and sand gave on an average 255 lbs. per square inch at fourteen days, 291 at twenty-eight days, 299 at three months, and 348 lbs. at six months. With two parts of sand the briquettes broke at 123, 166, 185, and 242 lbs. respectively. Another series of tests was instituted by Mr. Carey to show the effect upon the strength of the cement of using sea water alone, and diluted with distilled water, or concentrated by partial evaporation.

The following table gives the result, the mean of six tests in each case, using 20 per cent. of water and neat cement:—

TEST BRIQUETTES, 1" × 1", MADE UP WITH SALT WATER.

Water.	1 month.	2 months.	3 months.	6 months.	9 months.	12 months.
Fresh water,	525	525	750	900	949	678
½ distilled water,	537	542	690	650	965	592
½ sea water,	542	550	620	750	950	575
¼ distilled water,	542½	563	590	580	890	605
¼ sea water,	541	540	800	850	970	495
Sea water, 25 per cent. evaporated,						
Sea water, 50 per cent. evaporated,						

Mr. Carey states that the cement was not checked or cracked in any way, but in the case of both series of experiments was sound and well burnt. It was so ground as to leave a residue of about 10 per cent. on the 50 × 50 mesh sieve. The most noticeable feature in the above table is the remarkable effect of using strong brine, as evinced by the excellence of the tests at 3, 6, and 9 months, and the singular falling off in tensile strength of all the samples at the end of the 12 months, pointing, we should think, to some defect in the constitution of the cement. It would have been interesting to know how the cement behaved after the lapse of two or more years.

As Mr. Carey remarks, "the real point at issue is whether the salts of magnesia, which are admittedly deposited from the sea in porous concrete structures, are or are not inert." Arguing from the fact that magnesian limestone when used in large cities, where the rain brings down sulphate of ammonia, is chemically acted upon, and decomposed into magnesium sulphate, which latter is deposited in the form of crystals, and causes disintegration, he advises that in situations where ammonia may be brought into contact with concrete, it is desirable to use fresh water for gauging, and to discard cements containing a high percentage of magnesia. On the other hand, concrete made of sound and well burnt cement, varying from $\frac{1}{2}$ to $\frac{1}{4}$ part by volume and gauged with sea water, has been used for many existing structures in the sea, which have exhibited no signs of deterioration throughout a long term of years. There is, he thinks, "no conclusive evidence to prove that the precipitates from sea water induce disintegration of even fissured or porous concrete" when sound cement has been employed.

In the Aberdeen concrete it is clear that free caustic lime was present and was washed out of the concrete, while magnesia, in the form of magnesium hydrate, was precipitated, leading to the elimination of lime as calcium chloride and sulphate, but we learn nothing more from these facts than that lime is an unstable and soluble body, and that it should not form any considerable proportion of a durable concrete. The experience of Aberdeen has proved in fact this much and no more:—That "an

excess of caustic lime or caustic magnesia causes (1) disintegration by the expansion due to hydration, and that (2), being soluble, these substances, when conditions are favourable, may be washed out, leaving the concrete in a honey-combed state."

Mr. Smith devotes his attention entirely to the works at Aberdeen, and after a brief account of the concrete construction of the docks, he points out that immediately after completion considerable leakage was noticed coming through the concrete walls, and that soon after the entrance walls began to swell, some of the large blocks showing signs of bulging. As the damage appeared to be due to chemical action in the Portland cement, Prof. Brazier, of Aberdeen University, was consulted on the subject, and in a report dated June, 1887, he confirmed this opinion. He states that :—

"The analyses of the series of decomposed cements show a remarkable difference to the original cement, inasmuch as in all these samples there is found a large quantity of magnesia, and a large proportion of the lime in the form of carbonate. I believe this alteration is brought about entirely by the action of sea water upon the cement. There is no other source for either the magnesia or the carbonic acid."

The following table shows the composition of the original cement, and of samples of the decomposed cements :—

CONSTITUENTS.	Original Cement, Dry.	Decomposed Cement from Wing Wall, south side, inside Cofferdam.	Decomposed Cement from Wing Wall, south side, back of Plaster Skin.	Cement from Entrance Wall, above Culverts, inside Dock.	Cement from Entrance Wall, above Culverts, inside Dock. Drippings.	Cement from South Breakwater, west side.
Alumina and oxide of iron, . . .	13.10	26.76	23.42	1.06	1.53	21.60
Silica,	20.92	18.04	19.55	1.33	1.81	17.81
Carbonate of lime,	8.18	6.61	15.78	45.72	35.42	33.08
Hydrate of lime,	11.26	30.54	16.94	27.85	17.17	..
Hydrate of magnesia, . . .	..	13.57	15.08	21.03	39.96	9.94
Sulphuric acid,	0.82	2.98	4.23	1.32	0.90	4.89
Magnesia,	0.33	..	..	..	..	12.68*
Soluble in water,	..	1.50	..	1.71	8.71	..
Caustic lime,	45.39	..	..	..	..	..
	100.00	100.00	100.00	100.01	100.00	100.00

We may observe with respect to these analyses that both in the case of the original cement and the deteriorated concrete there are many matters which we are quite unable to reconcile; the lime is, however, present in the cement in what we must deem to be a dangerous excess.

In addition to these analyses, Prof. Brazier carried out a series of experiments with specimens of the cement digested in various solutions. The cement for these tests was obtained by breaking down a briquette, sifting out and rejecting the fine powder, and reserving for trial pieces about the size of a large-grained shot. In each case, 200 grains of cement tied up in small muslin bags were suspended in 20 ozs. (1 imperial pint) of the various fluids—1. Distilled water. 2. Solution of magnesium chloride containing 31 grains, equivalent to 13.05 grains of magnesia, the average proportion of this salt found in sea water. 3. Solution of magnesium chloride of double the above strength, 62 grains to the pint. 4. Solution of magnesium sulphate, containing the same equivalent of magnesia as No. 2. 5. Solution of magnesium sulphate of

* Carbonate of magnesia.

double the above strength. 6. Sea water, specific gravity 1.026, containing magnesium salts equivalent to 18.37 grains of magnesia per imperial pint. 7. Sea water, duplicate specimen, and a solution of chloride of sodium—250 grains per imperial pint.

The cement samples remained in these various solutions for about three months, and it was then found that No. 1, the distilled water, was but little altered. In No. 2, nearly the whole of the dissolved magnesia had been removed, and the clear liquid contained 14.62 grains of lime per pint. No. 3 had also lost nearly the whole of its magnesia, its place being taken by 26.04 grains of lime. Very much the same action went on in the case of the magnesium sulphate solutions 4 and 5, except that the amount of magnesia removed from solution and replaced by lime was relatively smaller. In the sea water tests, again, the magnesia present had been to a great extent precipitated; No. 6 showing a loss of 14.16 grains, and No. 7, 14.72 grains. But little action took place with the salt solution No. 8. These experiments certainly appear to confirm the opinion expressed by Professor Brazier that the magnesium salts in the sea water have a dangerous action upon the lime compounds of the cement in question, but it must be borne in mind that we have no guarantee that the Portland cement itself was originally of good quality, and contained its lime in stable combination with the silica. The analysis of the original cement (which was unfortunately made from a stale sample) shows only that the percentage of lime was very high (63.1 if the water and carbonic acid are eliminated). The disappearance of the silica, iron, and alumina in the fourth and fifth specimens, given in our table on p. 285, is extremely puzzling.

Experiments made by Mr. Pattinson, of Newcastle-upon-Tyne, agreed in all respects with the above, and he suggested certain investigations, subsequently carried out by Mr. Smith, to test the permeability of cement concrete, as it was thought that the sea passing in and out through the porous concrete at every tide would hasten the destructive action. These experiments led Mr. Smith to formulate the following theories, viz. :—That in order to obtain an impermeable concrete (1) the cement must be finely ground; (2) it should not be weaker than 1 of cement to 6 of sand and stones; and (3) the concrete should have sufficient time to set (at least three months) before the application of the pressure, due to a column of sea water.

Professor Brazier, moreover, believed that the observed expansion of the concrete in question was due to the substitution of magnesium hydrate and calcium sulphate, for the lime therein originally combined with carbonic acid. Mr. Smith states apparently on his authority—"There is no doubt that in permeable concrete the whole of the lime forms a base on which carbonic acid and the salts contained in the sea water act chemically, that the resulting deposit occupies a larger space than the lime base, and that the force of chemical action exceeds the adhesive power of the cement, thus effecting the rupture of the mortar, and expansion of the mass of concrete."

It will be evident that a source of danger is herein indicated if we admit that the cement compounds, consisting of hydrated silicates of lime, and not to any great extent of free lime, or carbonate of lime, as assumed by Mr. Smith, are liable to be attacked and damaged by the salts found in sea water. Numerous instances are, however, on record where cement concrete has withstood for a long series of years the influence of sea water, not only under a great tidal range, but under the still more trying action of alternate periods of submersion in the sea, and exposure to the air. In many of the great dock and harbour works we have examples of Portland cement concrete, which for upwards of forty years have resisted most perfectly the

attacks of sea water, and there can be but little doubt in the minds of all unbiased observers that in a well-made sample of Portland cement, when once properly indurated as a hydrated double silicate of lime and alumina, we possess a material quite unacted upon by sea water. The failure of certain specimens of concrete can, we think, in every case be assigned either to mistakes in the manufacture, defects in the quality, or imperfections in the mode of using the cement.

Appendix C.—German Standard Tests.*

STANDARDS FOR THE UNIFORM DELIVERY AND TESTING OF PORTLAND CEMENT.

Explanation of What is understood by Portland Cement.—Portland cement is a material resulting from the calcination, carried to the point of incipient fusion, of an intimate admixture of lime and argillaceous substances as its essential components; such calcination being followed by the grinding of the product to the fineness of flour.

I. PACKAGES AND WEIGHT.

Portland cement must, as a rule, be packed in standard-sized casks weighing 180 kilogrammes gross, and 170 kilogrammes nett (397 lbs. and 375 lbs.), and in half-sized standard casks of 90 kilogrammes gross, and 85 kilogrammes nett (199 and 188 lbs.). The gross weight must be clearly marked on the casks.

If the cement is wanted in other sized casks or in sacks the gross weight must be plainly indicated in figures upon each package.

Leakages, as also variations in individual packages, must not exceed 2 per cent. The casks and sacks must bear, in addition to the weights, the name of the firm or the factory trade mark of the maker plainly indicated on each.

Facts in support of I.—Both in the interests of the purchaser, and also to ensure sound business, the adoption of a uniform weight (for packages) is urgently required. For this purpose, by far the most usual, and as respects the commercial world, the almost universal weight of 180 kilogrammes tare = about 400 lbs. English has been selected.

II. TIME NEEDED TO SET.

In accordance with the purpose for which it is required Portland cement may be furnished to set either slowly or rapidly.

Such cements are to be regarded as slow-setting, which take two hours and more to become set.

Explanations to II.—In order to determine the period needed to set, in the case of slow-setting cements, a sample of the neat cement is stirred for three minutes with water into the form of a stiff paste, but for quick-setting cements the stirring is to be for one minute only. The mixture must then be spread on a glass plate at a single operation in the form of a pat about $1\frac{1}{2}$ centimetres ($\frac{1}{2}$ inch) thick, but thinning out at the edges. The consistency of the cement paste needed for this pat is to be such that when placed upon the plate, with a spatula, a few taps upon the glass suffice to cause the mass to flow out to a thin edge; for this purpose from 27 to 30 per cent. of water will generally suffice. As soon as the pat has become hard enough to withstand a gentle pressure with the finger-nail the cement is to be

* This translation was made by the Author of the First Edition of this work, in which edition it was first published in 1895.

regarded as having become set. In order to ascertain precisely the setting time, and to determine the beginning of the set, which (as the cement must be worked up before the set begins) is a matter of importance in the case of quick-setting cements, a normal needle of 300 grammes (10½ ozs.) weight is employed, which has a flat end with a superficial area of 1 square millimetre (0.015 square inch). This surface being at right angles to the axis, a metal ring of 4 centimetres in height and 8 centimetres in clear diameter (1½ inches and 3 inches) is placed on a glass plate, filled with cement paste, gauged as above, and placed beneath the needle. The interval of time which elapses between the gauging and that when the needle is no longer able to penetrate the entire depth of the paste, is regarded as that needed for the beginning of the set, and the time which expires until the needle will no longer produce any noteworthy impression on the hardened surface is the time required for the set. As the setting of cement is influenced by the air-temperature and by that of the water used for gauging purposes, in that the higher is the temperature the more rapid is the set, and the lower the temperature the longer is the time needed for setting, it is advisable, in order to obtain uniformity in the results, to conduct the observations at a mean temperature of air and water of from 15° to 18° Celsius (59° to 64.4° F.).

During the set there should be no perceptible evolution of heat in the case of slow-setting cements, while, on the other hand, quick-setting cements may manifest a notable increase in temperature.

Portland cement becomes by long storage slower in set, and increases in tensile strength, if it be kept in dry places, free from draughts. The still widely prevailing opinion that Portland cement deteriorates in quality by long keeping is, therefore, erroneous, and contract clauses which specify the employment only of fresh cement should be abandoned.

III. FREEDOM FROM CHANGE IN VOLUME.

Portland cement must be constant in volume. The decisive test of this quality shall be that a pat of neat cement, placed on a glass plate and protected from too rapid drying, immersed in water at the end of twenty-four hours, and kept under constant observation for a longer period, shall manifest no tendency to crumble or to show signs of splitting at the edges.

Explanations to III.—In carrying out this test, the pat prepared to determine the time needed for setting should, after the lapse of twenty-four hours in the case of slow-setting cements, but in any case only after the pat has become set, be placed in water. In the case of quick-setting cements, the pats may go into water in an even shorter period of time. The pats of slow-setting cement must, until they shall have become set, be protected from draughts and sunshine; this may best be done by putting them into a covered box, or by placing them beneath a damp cloth. By this means the formation of hair-cracks, due to shrinkage in rapid drying, will be avoided; such cracks generally appear in the centre of the pat, and are liable to be mistaken by unskilled observers for cracks caused by blowing.

If during the process of induration under water any crumbling takes place, or if cracks become manifest, this undoubtedly denotes the blowing of the cement; that is to say, that in consequence of its volumetric expansion the cement becomes cracked and a gradual disintegration of the first-formed cohesion takes place, which may ultimately lead to the complete disruption of the mass. The indications of blowing generally become apparent in the pats after about three days, but at all events observations extending over twenty-eight days are sufficient.

IV. FINENESS OF GRINDING.

Portland cement is to be so finely ground that the residue from a sample of the same passed through a sieve of 900 meshes per square centimetre (5,806 per sq. inch, or 76 per lin. inch) shall not exceed 10 per cent. The diameter of the sieve wire should be equal to half the clear opening of the mesh.

Explanations to IV.—In the case of each sieve test 100 grammes (0.22 lb.) of cement are to be used.

As cement is in nearly every instance employed with sand, and in some cases with large proportions of sand, while the cohesive strength of a sample of mortar is greater just in proportion as the cement is finely ground (because under these circumstances more particles of the cement come into action), the fineness of the grinding is of the utmost importance. It appears, therefore, to be evident that the fineness of the particles should be uniformly checked by the use of a fine sieve of the above number of meshes to the inch. It would, however, be misleading if the quality of a cement were to be determined alone by the fineness of the grinding, for inferior tender-burned cements are much oftener found to be well ground than good hard-burnt cements. The latter will, however, even if coarsely ground, possess a greater cohesive strength than the former. If the cement is to be used mixed with lime, it will be expedient to employ hard-burnt cements extremely well ground, the relatively high cost of which will be compensated for by the manifest improvement of the mortar.

V. TEST TO ASCERTAIN THE STRENGTH OF THE CEMENT.

The cohesive strength of Portland cement must be ascertained by testing a mixture of cement and sand. The testing should take place upon a uniform system both in tension and compression, and should be carried out with test samples of the same shape and sectional area, and with similar apparatus.

Together with these tests it is expedient also to ascertain the cohesive strength of the neat cement.

The tensile tests are to be carried out with briquettes, having a sectional area at the point of fracture of 5 square centimetres (0.775 square inch); in the tests for compression cubes should be used, having sides 50 square centimetres in area (7.75 square inches).

Facts in support of V.—As it is impossible uniformly to pronounce an opinion upon the cohesive strength of a sample of cement when employed with sand by means of experiments conducted with that cement without sand, particularly when it becomes necessary to compare the cements of different makers, it is, therefore, imperative to test the cement along with sand.

The testing of neat cement is to be advocated when it is required to prove the value of Portland cement as compared with mixed cements and other hydraulic binding materials, because, on account of its high tensile strength when used neat, in which respect it surpasses all other similar materials, it shows to greater advantage tested thus than when tested with sand.

Although the proportional strength under compression and under tension differs in the case of various binding agents, it is, nevertheless, customary to employ the tensile strength as indicative of the value of the different hydraulic cements. This, however, leads to an unfair valuation of their properties. And further, whereas in all practical applications of mortar the resistance to compression is the first consideration, it is only these latter tests which can be relied upon to furnish really conclusive results.

To secure the necessary uniformity in the tests it is advisable to make use of the same description of testing apparatus and tools as those employed in the Royal Testing Station at Charlottenburg, Berlin (see Fig. 57, p. 223).

VI. TESTS UNDER TENSION AND COMPRESSION.

Slow-setting Portland cement shall, when tested with 3 parts by weight of standard sand, after a period of twenty-eight days induration—one day in air and twenty-seven days in water—attain a minimum tensile strength of 16 kilogrammes per square centimetre (227 lbs. per square inch). The strength under compression shall be at least 160 kilogrammes per square centimetre (2,275 lbs. per square inch). In the case of quick-setting cements the tensile strength after twenty-eight days is generally inferior to the above. It is, therefore, necessary, when stipulating the amount of tensile strength, to indicate also the time needed for the set.

Explanations.—As different cements may vary very considerably as respects their power to unite sand, upon which property their industrial application mainly depends, it is imperatively necessary, in the comparison of several samples of cements, to test them with a large proportion of sand. It is assumed that the most suitable proportion for this purpose is 3 parts by weight of sand to 1 part of cement. Since it is with 3 parts of sand that the binding power of the cement comes adequately into play.

Cement which exhibits a greater relative tensile strength as compared with the crushing strain often manifests a superior capacity for uniting sand, and merits for this reason, as likewise for its greater strength with an equal amount of sand, to command an increased selling price.

The standard test under compression is that after twenty-eight days, since it is not possible when comparing several kinds of cements to properly ascertain the binding capacity in a shorter period of time. Thus, for instance, after twenty-eight days the tests of different samples of cements in compression may be alike, whereas, after seven days only, there were important differences. The tensile strength at twenty-eight days constitutes the decisive test on delivery of the cement. If, however, a check-test at seven days is needed, this may be secured by a preliminary test when the ratio of tensile strength after seven days to that at twenty-eight days in the case of any given sample of cement has been determined. This preliminary test may also be carried out with neat cement, when the proportionate strength of the neat cement to that with 3 parts of cement at twenty-eight days has been ascertained.

It is advisable in all cases, when there is a possibility of so doing, to extend the tensile tests over a longer period, by means of cement samples prepared beforehand for this purpose, in order to learn the behaviour of various cements during a longer period of induration.

To attain uniformity in the results, it is in all cases necessary to employ sand having grains of the same size and of the same quality. This normal sand is prepared as follows:—The purest possible quartz sand is washed, dried, and passed through a sieve of 387 meshes per square inch to eliminate the coarser particles, and then through one of 774 meshes per square inch to remove the finer particles. The thickness of the wires not to exceed 0.015 inch and 0.012 inch respectively.

As all samples of quartz sand when treated in the same way do not manifest the same cohesive strength, it is necessary to ascertain whether the specimen of normal sand employed gives uniform tensile tests with those shown in the case of the sand supplied for testing purposes under the authority of the German Cement Manufacturers' Association, which sand is also used at the Royal Testing Station at Charlottenburg, Berlin.

Description of the Tests employed to ascertain the Tensile and Cohesive Strength.—As it is important to secure absolute uniformity in the results in testing the same cement in different places, it is imperatively necessary to adhere most strictly to the rules that are here indicated. In order to obtain correct averages at least ten test pieces must be prepared for each set of experiments.

PREPARATION OF THE CEMENT WITH SAND TEST-PIECES.

Tensile Tests.—The tensile test-pieces may be prepared either by hand or by mechanical means.

(a) *By Hand Work.*—On the sheet of metal, or thick glass, serving for the formation of the test-pieces, must be placed five pieces of blotting-paper saturated with water, and on these are laid the five moulds, also rinsed out with water. Then 250 grammes (8.8 ozs.) of cement and 750 grammes (26.4 ozs.) of dry normal sand are weighed out, and well mixed together in a basin. To this mixture must now be added 100 c.c. = 100 grammes (3.52 ozs.) of pure fresh water, and the whole mass is then briskly stirred for five minutes. The five moulds are then filled with the mortar thus prepared, which is pressed into them, and well heaped up into a curved form above the top. By means of an iron spatula, having a surface of $2\frac{1}{8} \times 1\frac{1}{8}$ inches, 13 inches in length, and weighing $7\frac{1}{4}$ ozs. (Fig. 55, p. 217), the mortar is tapped softly near the edges to begin with, and then gradually harder, so as to drive it down into the mould, until the whole mass becomes elastic, and water appears on the surface. It is absolutely necessary to continue the process of the filling-in of the moulds until this stage is reached, which will need about one minute per mould. It will not do to introduce a second supply of mortar and to beat that down, because it is essential to keep the test-pieces made with the same kind of cement at different testing stations identical in point of density. The superfluous cement is then struck off with a knife, and the surface is polished over with the same. Then the mould is carefully removed, and the test-pieces are placed in a box, lined with zinc and provided with a cover, in order to avoid unequal desiccation, caused by variations in the temperature. Twenty-four hours after they are made, the test-pieces must be placed in water, and care must be taken to keep them covered with water during the whole period of induration.

(b) *Preparation by Mechanical Means.*—After the mould, with the filling-box attached to it, has been securely fastened to the bottom plate by means of the two thumb-screws, 180 grammes of the mortar, prepared as in the foregoing instructions (a), are introduced into the mould for each test, and the iron moulding core is placed in position. Then, by means of Dr. Böhme's percussion apparatus, having a hammer weighing 4.4 lbs., 150 blows are imparted to the core.

After the removal of the filling-box and the core, the test-piece is struck off level and polished as before; then taken off in the mould from the bottom plate, and dealt with as in the case of (a), above.

By careful attention to the foregoing rules, hand-made test-pieces and those prepared mechanically give fairly uniform results. In disputed cases, however, tests made by mechanical means must be regarded as decisive.

Tests under Compression.—In order to secure uniformity in the results of testing by compression carried out at various testing stations, it is necessary to have recourse to mechanical preparation of the tests.

Fourteen ounces of cement are weighed out and well mixed in a basin with 42 ozs. of dry normal sand. 160 c.c. = 5.63 ozs. water are then added, and the compound is briskly stirred into mortar for five minutes. Then 30 ozs. of this

mortar are inserted into the cubical mould, having the filling-box attached, the whole being securely fastened by screws to the bottom plate. The iron core is placed in the mould, and is caused to receive 150 blows from Dr. Böhme's percussion apparatus with a hammer weighing 4.4 lbs. After the removal of the filling-box and the core, the test-block is struck off and polished, taken off the bottom plate in the mould, and dealt with as in the case of (a), above.

Preparation of Test-Pieces of Neat Cement.—The moulds are slightly oiled on the inner surface, and placed on the metal or glass plate (without any blotting-paper under them). Then 35.2 ozs. of cement are weighed out, and to this is added 7 ozs. = 200 c.c. of water, and the whole are well stirred for five minutes (this is best done with a pestle), filled into the moulds, so as to be well heaped up above the surface, and then dealt with as in (a). The moulds can, however, only be removed when the cement is sufficiently set.

As, during the ramming in of the neat cement, the aim is to produce test-pieces of the same consistency, the added water must be proportionately increased in the case of very finely-ground or quick-setting cements.

The amount of water employed must always be indicated when stating the figures representing the tensile strength.

Method of Carrying Out the Tests.—All test-pieces must be tested immediately they are taken out of the water. As the time taken to apply the load has an influence upon the result, the weight should, in the case of tensile tests, be increased at the rate of 3.52 ozs. per second. The mean of ten tests is to be taken as the ascertained tensile strength. In carrying out the compression tests, in order to obtain strictly comparative results, the pressure must always be exerted on two opposite sides of the cube, not on the base and smooth top. The mean of ten tests shall be taken as the ascertained strength under compression.

Appendix D.—Report of a Committee of the American Society for Testing Materials on a Standard Specification for Cement.

Standard Specifications for Cement.

1. *General Observations.*—These remarks have been prepared with a view of pointing out the pertinent features of the various requirements and the precautions to be observed in the interpretation of the results of the tests.

2. The committee would suggest that the acceptance or rejection under these specifications be based on tests made by an experienced person having the proper means for making the tests.

3. *Specific Gravity.*—Specific gravity is useful in detecting adulteration or underburning. The results of tests of specific gravity are not necessarily conclusive as an indication of the quality of a cement, but when in combination with the results of other tests may afford valuable indications.

4. *Fineness.*—The sieves should be kept thoroughly dry.

5. *Time of Setting.*—Great care should be exercised to maintain the test pieces under as uniform conditions as possible. A sudden change or wide range of temperature in the room in which the tests are made, a very dry or humid atmosphere, and other irregularities vitally affect the rate of setting.

6. *Tensile Strength.*—Each consumer must fix the minimum requirements for tensile strength to suit his own conditions. They shall, however, be within the limits stated.

7. *Constancy of Volume.*—The tests for constancy of volume are divided into two classes—the first normal, the second accelerated. The latter should be regarded as a precautionary test only, and not infallible. So many conditions enter into the making and interpreting of it that it should be used with extreme care.

8. In making the pats the greatest care should be exercised to avoid initial strains due to molding or to too rapid drying-out during the first twenty-four hours. The pats should be preserved under the most uniform conditions possible, and rapid changes of temperature should be avoided.

9. The failure to meet the requirements of the accelerated tests need not be sufficient cause for rejection. The cement may, however, be held for twenty-eight days, and a re-test made at the end of that period. Failure to meet the requirements at this time should be considered sufficient cause for rejection, although in the present state of our knowledge it cannot be said that such failure necessarily indicates unsoundness, nor can the cement be considered entirely satisfactory simply because it passes the tests.

Standard Specifications for Cement.

1. *General Conditions.*—All cement shall be inspected.

2. Cement may be inspected either at the place of manufacture or on the work.

3. In order to allow ample time for inspecting and testing, the cement should be stored in a suitable water-tight building having the floor properly blocked or raised from the ground.

4. The cement shall be stored in such a manner as to permit easy access for proper inspection and identification of each shipment.

5. Every facility shall be provided by the contractor, and a period of at least twelve days allowed for the inspection and necessary tests.

6. Cement shall be delivered in suitable packages with the brand and name of manufacturer plainly marked thereon.

7. A bag of cement shall contain 94 lbs. of cement net. Each barrel of Portland cement shall contain four bags, and each barrel of natural cement shall contain three bags of the above net weight.

8. Cement failing to meet the seven-day requirements may be held awaiting the results of the twenty-eight-day tests before rejection.

9. All tests shall be made in accordance with the methods proposed by the Committee on Uniform Tests of Cement of the American Society of Civil Engineers, presented to the Society, January 21, 1903, and amended January 20, 1904, with all subsequent amendments thereto.

10. The acceptance or rejection shall be based on the following requirements:—

Natural Cement.

11. *Definition.*—This term shall be applied to the finely pulverised product resulting from the calcination of an argillaceous limestone at a temperature only sufficient to drive off the carbonic acid gas.

12. *Specific Gravity.*—The specific gravity of the cement thoroughly dried at 100° C. shall be not less than 2.8.

13. *Fineness.*—It shall leave by weight a residue of not more than 10 per cent. on the No. 100, and 30 per cent. on the No. 200 sieve.

14. *Time of Setting.*—It shall develop initial set in not less than ten minutes, and hard set in not less than thirty minutes, nor more than three hours.

15. *Tensile Strength*.—The minimum requirements for tensile strength for briquettes 1 inch square in cross section shall be within the following limits, and shall show no retrogression in strength within the periods specified :—

NEAT CEMENT.			
Age.			Strength.
24 hours in moist air,	.	.	50-100 lbs.
7 days (1 day in moist air, 6 days in water),	.	.	100-200 „
28 „ (1 „ 27 „),	.	.	200-300 „

ONE PART CEMENT, THREE PARTS STANDARD SAND.

7 days (1 day in air, 6 days in water),	.	.	25-75 lbs.
28 „ (1 „ 27 „),	.	.	75-150 „

16. *Constancy of Volume*.—Pats of neat cement about 3 inches in diameter, $\frac{1}{4}$ inch thick at centre, tapering to a thin edge, shall be kept in moist air for a period of twenty-four hours.

(a) A pat is then kept in air at normal temperature.

(b) Another is kept in water maintained as near 70° F. as practicable.

17. These pats are observed at intervals for at least twenty-eight days, and, to satisfactorily pass the tests, should remain firm and hard and show no signs of distortion, checking, cracking, or disintegrating.

Portland Cement.

18. *Definition*.—This term is applied to the finely-pulverised product resulting from the calcination to incipient fusion of an intimate mixture of properly-proportioned argillaceous and calcareous materials, and to which no addition greater than 3 per cent. has been made subsequent to calcination.

19. *Specific Gravity*.—The specific gravity of the cement, thoroughly dried at 100° C., shall be not less than 3.10.

20. *Fineness*.—It shall leave by weight a residue of not more than 8 per cent. on the No. 100, and not more than 25 per cent. on the No. 200 sieve.

21. *Time of Setting*.—It shall develop initial set in not less than thirty minutes, but must develop hard set in not less than one hour, nor more than ten hours.

22. *Tensile Strength*.—The minimum requirements for tensile strength for briquettes 1 inch square in section shall be within the following limits, and shall show no retrogression in strength within the periods specified :—

NEAT CEMENT.			
Age.			Strength.
24 hours in moist air,	.	.	150-200 lbs.
7 days (1 day in moist air, 6 days in water),	.	.	450-550 „
28 „ (1 „ 27 „),	.	.	550-650 „

ONE PART CEMENT, THREE PARTS SAND.

7 days (1 day in moist air, 6 days in water),	.	.	150-200 lbs.
28 „ (1 „ 27 „),	.	.	200-300 „

23. *Constancy of Volume.*—Pats of neat cement about 3 inches in diameter, $\frac{1}{2}$ inch thick at the centre, and tapering to a thin edge, shall be kept in moist air for a period of twenty-four hours.

- (a) A pat is then kept in air at normal temperature and observed at intervals for at least twenty-eight days.
- (b) Another pat is kept in water maintained as near 70° F. as practicable, and observed at intervals for at least twenty-eight days.
- (c) A third pat is exposed in any convenient way in an atmosphere of steam, above boiling water, in a loosely-closed vessel for five hours.

24. These pats, to satisfactorily pass the requirements, shall remain firm and hard and show no signs of distortion, checking, cracking, or disintegration.

25. *Sulphuric Acid and Magnesia.*—The cement shall not contain more than 1.75 per cent. of anhydrous sulphuric acid (SO_3), nor more than 4 per cent. of magnesia (MgO).

Appendix E.—The Cost of Cement Manufacture.

It may not be wholly amiss in a work of this character if we devote a few remarks to the cost of the manufacture of cement, a subject of great importance at the present time, and one which has necessarily attracted a vast amount of attention. There can be no two opinions that many of the older works are so heavily weighted with capital, representing obsolete appliances, imperfect processes of manufacture, and money thrown away upon past failures, that these “dead expenses” severely handicap them in competing with modern works, constructed upon the most economical lines, and provided with all the requisite plant for the inexpensive handling of the raw materials. The cost of the raw materials may in itself constitute a more or less serious item in the balance sheet, and there can be no doubt that cement makers able to control their own supply of clay and chalk or limestone in the immediate vicinity of their works have a great advantage over those who have to bring their materials from a distance, or to obtain them at second hand. In certain parts of this country remote from the chalk formation, as, for instance, in the Tyne Districts, where fuel is relatively cheap, cement factories have been established, which depend for their supply upon chalk brought back as ballast in colliers. But these works find themselves severely handicapped in the competition with factories established on the Thames and Medway, close to the quarries. It may be taken for granted that most of the older works, which, as we have seen, cluster round the chalk districts south-east of London, where both Medway clay and chalk are abundant, can command unlimited supplies of raw materials at a price ranging from 2s. to 2s. 6d. per ton of finished cement. Even in those works where the chalk has to be bought, it can usually be laid down on the works at from 1s. 2d. to 1s. 6d. per ton; the clay costing in a similar way from 2s. 2d. to 2s. 8d. per ton. In the lias cement districts in the Midland Counties the cost of raw materials is relatively high, owing to the increased cost of quarrying the thin beds of stone under great depths of shale and clay. We know of one cement works successfully conducted in the Midlands, where the cost of the raw materials from the lias formation delivered on the site is set down at 4s. 6d. per ton. Even in the districts where the hard limestone takes the place of chalk, the stone can be quarried and laid down on the works for from 1s. 3d. to 1s. 9d. per ton. The price of fuel (coke

or coal) is also an important consideration to the cement maker, as this item amounts to about one-quarter of the total cost of manufacture, and cheap coke may outweigh the disadvantages due to relatively costly works or expensive raw materials. The carriage of Portland cement on the rail is another serious item, as most of the companies are in the habit of charging very high rates for cements, as compared with coal or stone. It may be taken as a general rule that no large works can be advantageously carried on, which have not direct communication with the rail by means of sidings, or which do not possess cheap water communication. The export trade in Portland is very extensive, but this business is almost entirely in the hands of makers on the Thames and Medway, or in the sea-port towns. The following estimates will give some idea of the items of expenditure under various heads in the manufacture of Portland cement.

The following analysis of the cost of cement making on the Medway was published in the *Portland Cement Journal* in 1892. It purports to give the exact figures "taken from actual accounts for the years 1890 and 1891." There is no provision made for interest on capital, which is stated to have been over £40,000 for buildings and plant, and represents rather a large, but by no means an unusual expenditure for this output. The property is freehold, and the sum of £500 charged for depreciation only relates to the depreciation on fixed machinery and plant. No sum appears to be set down for agency or travelling, bad debts, and incidental losses, and it is stated with respect to cost of chalk, clay, coal, and coke, that the figures given do not include labour thereon after reaching the wharf, such labour being included in the wages item :—

	1890.	Cost per ton of finished cement.	1891.	Cost per ton of finished cement.
Quantity of cement made in tons,	21,336		20,175	
Chalk and freight,	2,326	Shillings. £	2,571	Shillings. £
Clay and freight,	598	2.180	691	2.549
Coal and freight,	4,935	.656	5,960	.686
Coke and freight,	5,087	4.626	5,562	5.923
Wages,	6,457	4.722	6,408	5.513
Rates and Taxes,	170	6.063	170	6.353
Repairs, materials, and wages (on repairs),	1,197	.159	1,761	.168
Stores, oil, grease, firebricks, iron, steel, &c., not charged to repairs,	1,133	1.123	1,151	1.726
Trade charges, postage, stationery, &c.,	86	1.068	93	1.141
Insurance,	85	.081	79	.092
Depreciation, amount written off fixed machinery and plant,	500	.081	500	.073
Manager,	250	.468	250	.496
Books kept in London, salaries, stationery, &c., proportion charged,	195	.234	218	.248
		.188		.216
Add to wages, say, for cement in casks, 5,000 tons at 1s. 4½d.,	£22,964	21.529 = 1.396	£25,436	25.193 = 1.396
		22.925 = 23/		26.589 = 26/7

From our experience of the cost of raw materials in the London district, we regard the average cost of chalk and clay on the wharf for the two years amounting to 2.985s., or, as nearly as possible, 3s. per ton of finished cement, as rather too high, and the charge for fuel is certainly extravagant, amounting as it does to over 10s. 4d. per ton of cement. It will be noticed that the prices of 1891 are more than 25 per cent. higher than those of 1890. It is stated that the average selling price of the

cement at the works was 28s. 6d. per ton in 1892, and it will thus be seen that the manufacture was being conducted at an actual loss, if proper provision is made for the items to which we have called attention. In the face of the above figures, it can easily be understood that the Portland cement trade is in a very bad state, and that many of the large concerns are paying no dividend.

It will readily be understood that the publication of an estimate of this kind evoked considerable criticism, and shortly afterwards another estimate was published which emanated from a correspondent, who stated that he could erect works in the Medway district, on certain new lines, capable of producing 35,000 tons of cement a year, at a cost of 16s. 9d. per ton. He proposed to erect the manufactory in question on freehold land, to be acquired on advantageous terms, the expense of which land, together with the outlay on the erection of the necessary buildings, was not to exceed £20,000. This sum does not appear to include the cost of the machinery and plant. It will be seen that in this analysis, while the cost of the raw materials delivered on works is 2s. 8d. per ton of cement, that of the fuel amounts only to 5s. 6'3d., as compared with 3s. and 10s. 4d. respectively, the mean of the figures previously given in each case. The wages are about the same in each estimate.

Cost of Manufacture of 35,000 tons of Cement on the Medway.		Materials.		Wages.
52,500 tons of chalk alongside wash-mill, . . .	1/4	£3,062 10 0		
17,500 tons of clay alongside wharf and landing, . . .	1/10	1,604 8 4	1/4	£291 13 4
70,000 tons into wash-mill, . . .			3/8	375 0 0
1,650 tons of Welsh coal delivered, . . .	20/	1,650 0 0	1/4	27 10 0
13,000 tons of coke and faggots, . . .	12/4	8,016 13 4	3/8	433 13 4
Repairs and renewals, . . .	3/8	1,166 13 4	1/4	583 6 8
Stores, oil, grease, timber, and other sundry goods, . . .	1/6	875 0 0		
Burning—including filling 1/6, drawing 1/6, . . .	..	..	2/	3,500 0 0
Miller wet 1/2, dry 4/1, . . .	..	..	3/8	875 0 0
Sundries—(labour) engineer 60/, man 30/, drivers 80/, stoker 25/, sampler 30/, watchman and house 20/, tallow 25/, two odd men 40/, bags 20/, one night driver 30/, stoker 25/, man 40/. Total £20 5/ per week for 52 weeks, . . .	..	..		1,053 0 0
Coals and sacks, filling, heading, and loading, . . .	..	..	1/4	2,333 13 4
Rates and taxes 1/2, trade charges and stationery, 1 1/2, . . .	3/4	510 8 4		..
Insurance—Boiler, fire, and Liability, . . .	1/	145 16 8		..
Depreciation fund, fixed buildings and plant, . . .	1/4	583 6 8		..
Manager and clerk, . . .	..	..		500 0 0
Allow per contingencies, . . .	3/8	487 10 0	3/8	875 0 0
Materials = 10/3'78 per ton.		£18,062 1 8		£11,347 16 8
Wages = 6/5'81 ,,				18,052 1 8
Total, . 16/9'79 ,,				£29,399 18 4

By way of comparison with these estimates, we insert an analysis of the cost of producing cement by the semi-dry process in a works in the lias district. The stone here is relatively costly, but fuel is cheaper than nearer London. In consequence of the heavy outlay incurred upon the repair of the works, which were kept in a high state of efficiency, by constant renewals, this item appears excessive. It will be seen that the total cost of manufacture after the repayment of 5 per cent. on a rather heavy capital was under 25s. per ton, or deducting interest 22s. 9d. per ton, and this is about the figure we should set down for a well managed works in the South of England. We understand, on the Continent, where fuel is dear and where the cement is very well ground, that in works in which a hard limestone is used the expense of making Portland cement can be kept well within these figures.

COST OF PORTLAND CEMENT MANUFACTURE IN THE MIDLANDS.

Capital for land, buildings, and plant, £21,000.

Amount of cement made in tons, 9,360.

		Per ton of cement.
	£ s. d.	s. d.
Raw material—limestone, shale, and royalty,	1,867 10 0	3 9
Coal and coke,	2,622 0 0	5 3-2
Oil, grease, and small stores,	540 0 0	1 1
Wages,	3,590 0 0	7 2-5
Management,	525 0 0	1 0-6
Agency, advertisements, &c.,	232 0 0	0 6-8
Repairs, materials, and wages on repairs,	1,320 0 0	2 8
Office printing, stationery,	180 0 0	0 4-5
Rates and taxes,	70 0 0	0 1-7
Bad debts,	27 10 0	0 0-6
Interest on capital at 5 per cent.,	1,060 0 0	2 1-3
Depreciation on machinery and plant,	225 0 0	0 6-3
Insurance—buildings, boilers, and workmen,	56 0 0	0 1-3
Cost = nearly 25s. per ton of cement.	£12,366 0 0	24 10-8

Appendix F.—Dorking Stone Lime.

Writers on building materials and the authorities who are responsible for all our most carefully drawn specifications have, with a surprising degree of unanimity, concurred in calling the lime prepared from the lower chalk in the vicinity of Dorking a "stone lime." We have sought for some explanation of this fallacy, and offer the following suggestion:—Certain of the beds near Betchworth, and in the chalk hills eastward of Dorking, are much indurated and discoloured with iron salts, and a bed just between the chalk and the gault, known as firestone, is very hard, and is locally used for building. This indurated chalk is rejected by the lime burners as, owing to the high percentage of silica and alumina present therein, it yields a poor and very sluggish lime, but the raw material has certainly some pretensions to be called a stone. The lime prepared round Dorking is all burnt from chalk which contains from 5 to 10 per cent. of clay, and is of a pleasant buff tint. Even Bartholomew, writing in 1840, is careful to point out that the "stone lime" of Dorking should be specified, and his precepts are still diligently followed at the present day by the conscientious architect who knows what he wants for the preparation of a good sample of mortar.

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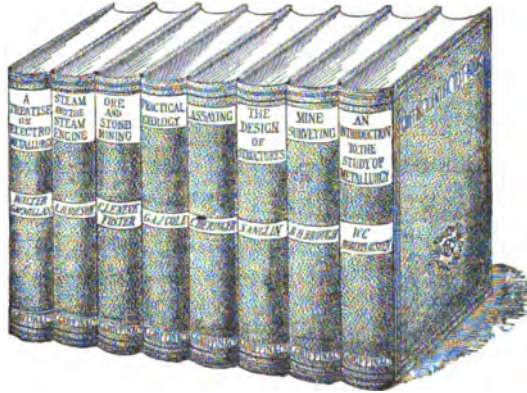
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